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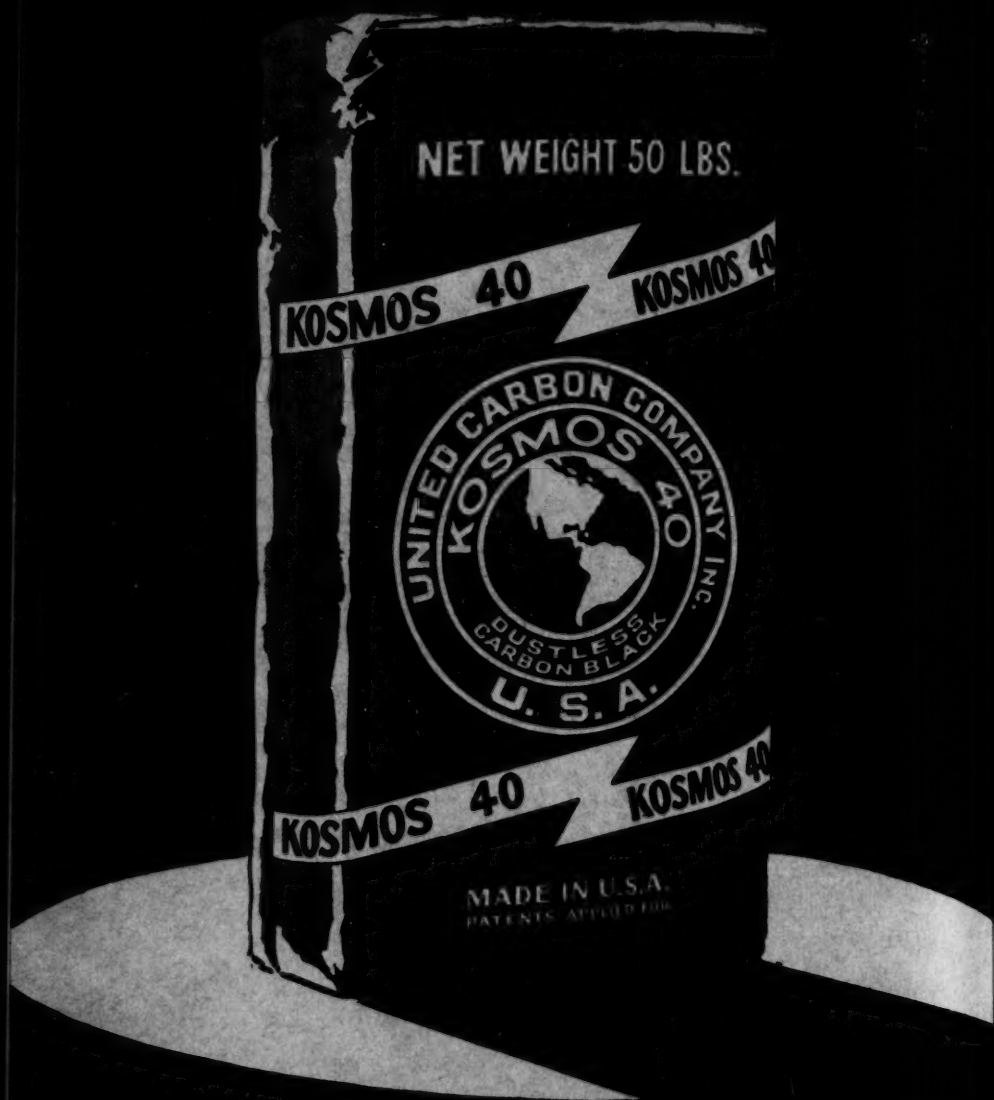
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RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XX

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October, 1947

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

RECLAIMED RUBBER—THE STORY OF AN AMERICAN RAW MATERIAL. By J. M. Ball. With Forward by William Welch, and Epilogue by Fred Traflet. Published by the Rubber Reclaimers Association, Inc., New York, 1937. 6 × 9 in. 248 pp. Price \$5.00.—The early days of natural rubber furnished many incidents which lend themselves to romantic treatment, such as the trials and triumphs of Charles Goodyear and the adventures of Sir Henry Wickham, and full advantage has been taken of these to popularize the history of crude rubber. On the other hand, few outside the rubber industry have ever heard of reclaim, while to those whose lot it is to use it daily, it is no more than an uninteresting and uninspiring ingredient in their mixings.

In J. M. Ball, however, reclaim has found a worthy historian, one who has set himself to know the facts, to know the people who made the facts, and to present all before the reader in a thoroughly reliable and enjoyable account. He has had the advantage of the willing coöperation of firms and of individuals connected with his story. From his wealth of material and experience he has

made a most judicious selection, building up a fully satisfying picture, yet without burdening the reader with a mass of detail.

As is natural, the beginning and early growth of reclaiming are given prominence, especially the inside story and patent actions involved in the development of the acid and the alkali processes, the whole being told almost as much in the words of the original actors in the scene, in the form of a wise and skillful selection of quotations from original documents, as in the writer's own words. An account of more modern discoveries, including war-time methods of recovery of scrap rubber, rounds out the whole.

The technical account of present-day practice in reclaim manufacture has its value considerably increased by the inclusion of a series of good illustrations. The uses of reclaim in rubber goods manufacture are likewise detailed.

Nor are the commercial and economic angles neglected. Company history is included, and there is a useful chapter on statistics. An adequate bibliography and index complete the book. As may be gathered from the subtitle, the treatment deals almost wholly with the American scene, and very little is said as to British or Continental practice and contributions to reclaim technology.

The style, printing, binding, and paper are all in good taste, and combine to form a volume which is pleasant to see and handle as well as interesting and informative to read. [From *The Journal of Rubber Research*.]

A STUDY OF ACCELERATED AGING TESTS. British Ministry of Supply, Shell Mex House, Strand, London, W.C. 2, England. $6\frac{1}{4} \times 9\frac{1}{2}$ in. 16 pp.— Issued as part of the British Services Rubber Investigations, representing research carried out by the Imperial Chemical Industries, Ltd., at the request of the British Admiralty, this report is devoted to a study of accelerated aging tests, and contains recommendations for improving present testing technique. The summary and conclusions reached at the Birmingham Conference (a symposium held in Birmingham, England, on May 12, 1945, under the auspices of the Institution of the Rubber Industry) are given, as are the results of special investigations made at the I.C.I. laboratories in Blackley, Manchester. The recommendations for improving present technique cover general tests, atmospheric or ozone cracking tests, sunlight or accelerated light tests, and oven and bomb tests. [From *The Rubber Age* of New York.]

TECHNOLOGICAL AND PHYSICAL INVESTIGATIONS ON NATURAL AND SYNTHETIC RUBBERS. By A. J. Wildschut. Published by the Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y. $5\frac{1}{2} \times 8$ in. 172 pp. \$3.00.— Issued as part of the current series on the Progress of Research in Holland during the war, the purpose of which is to prove that scientists in the Netherlands remained active during the five years of German occupation, this monograph discusses investigations in the field of rubber and rubberlike materials carried out between the summer of 1939 and that of 1944. With some exceptions, the experimental work described was accomplished by the author and his coworkers. Wildschut is a research engineer of the Rubber Foundation at Delft.

Divided into two sections covering technological and physical investigations, respectively, the book consists of nine chapters, as follows: (1) Standard Measurements; (2) Miscellaneous Investigations; (3) Modification by Means of the Vulcanization Process; (4) Physical Methods in Structural Research; (5) Meas-

urements Concerning Plasticity and Elasticity of Vulcanized Rubber; (6) Mechanical Properties Under Special Circumstances; (7) X-Ray Investigations; (8) Some Electrical Investigations; (9) General Conclusions.

Some of the investigations were carried out under extremely difficult conditions, and the author stresses the fact that due to the war situation only a limited amount of literature was available for consultation. American and British literature was especially scarce. Nevertheless, the results reported should prove a valuable contribution to the technical literature of the industry. [From *The Rubber Age* of New York.]

MECHANISMS OF REACTIONS AT CARBON-CARBON DOUBLE BONDS. Charles C. Price. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. 1946. 128 pages. Tables and illustrations. Cloth, 6 × 9 inches. Price \$2.50.—“Chapters in Organic Chemistry” has been the vogue in many institutions ever since Alfred W. Stewart began the publication in 1908 of his series entitled “Recent Advances in Organic Chemistry”. It is impossible for anyone to keep up with the vast literature of organic chemistry; therefore the publication of brief résumés in special fields is very helpful and worthwhile. The biennial Organic Symposia of the American Chemical Society, the Chemical Research Conferences (formerly the Gibson Island Research Conferences), and special lectures at different universities are all evidence of this desirable trend. The present volume is the first of a new series of this general type although the series is not confined to organic chemistry alone, but to chemistry in general.

According to H. Mark, the editor, “Topics of special interest will be selected and presented in a manner that accentuates the personal aspect and scientific approach of the author and possible trends and future outlooks”.

The author, professor of chemistry at the University of Notre Dame, states, “This volume contains a series of lectures presented by the author at the Polytechnic Institute of Brooklyn during the eventful summer of 1945 . . . No pretense is made that the subject has been given the thorough treatment which, it is hoped, will one day be possible”.

This book is little in size, but hefty in material. The reader has to keep on his “thinking cap” if he hopes to digest and understand the subjects discussed therein.

The list of chapters shows the coverage of the subject: electronic structure of unsaturated organic molecules, ionic reactions involving double bonds, free radical reactions involving double bonds, free radical addition polymerization, copolymerization, emulsion and suspension polymerization, and polar polymerization.

The author discusses these subjects very directly and is not afraid to state both sides of an argument. “An alternative explanation is possible” is given or implied many times. When good evidence is available, he uses it to advantage. Some mathematical formulas are used here and there, but not enough to scare away the nonmathematical reader. There are many figures and tables and a great many structural formulae and equations.

As one reads this book, he finds so many different angles and viewpoints discussed that he is likely to become somewhat confused, but on finishing it he will surely feel, not only that much fine work is being done, but also that a grand order is coming out of the present apparent chaos. [H. L. Fisher in the *India Rubber World*.]

PHYSICAL CONSTANTS OF HYDROCARBONS. VOL. IV. POLYNUCLEAR AROMATIC HYDROCARBONS. By Gustav Egloff. Published by the Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6 × 9 in. 540 pp. \$17.50.—Continuing the arrangements made with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in 1919, under which the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, undertook the production and publication of Critical Tables of Chemical and Physical Constants, this latest volume of the series is a collation of all melting point, boiling point, density, and refractive index data available on polynuclear aromatic hydrocarbons. The principal source of these hydrocarbons is coal tar, but some of the compounds are also found in petroleum and other natural sources, and many are produced synthetically. The author points out in his preface that the thousands of known compounds reproduced in the volume represent only a small fraction of the theoretical possibilities. [From *The Rubber Age* of New York.]

FIRE AND EXPLOSION HAZARDS OF THE MANUFACTURE OF SYNTHETIC RUBBER. National Board of Fire Underwriters, 85 John St., New York 7, N. Y. 6 × 9 in. 36 pp.—Prepared by a special committee of the Advisory Engineering Council of the National Board of Fire Underwriters, this report covers butadiene, styrene and GR-S. It details the various fire and explosion hazards involved in the manufacture of both the raw materials and the polymer, and outlines specific safeguards against such hazards. A table covering the properties of various materials used in the manufacture of synthetic rubber is included, as is a nomenclature of terms pertinent to the field. [From *The Rubber Age* of New York.]

TECHNOLOGY OF ADHESIVES. By John Delmonte. Published by Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6 × 9 in. 516 pp. \$8.00.—Although from a quantity production viewpoint, adhesives are not far removed from the figures for molded parts and surface coating materials, they have been deemed insignificant in the past in comparison with the more colorful and utilitarian molded, laminated, and cast plastics. Developments in adhesives, however, have closely paralleled those in high polymers, and this book ties together the developments in plastics with those of adhesives.

The book is probably the most complete one yet issued which covers the technology of adhesives. After his introduction, including a classification of adhesives, the author treats with adhesives based on phenolic resins, urea and melamine resins, miscellaneous thermosetting resins, polyvinyl resins, polystyrene and acrylic resins, the thermoplastic synthetic resins, cellulose derivatives, protein substances, vegetable glues and natural resins, animal glues, and sodium silicate. In addition there are chapters devoted to theories of adhesive action; adhesives for wood, tapes, papers, cloths and foils; inorganic materials; tests and specifications; and the cementing of organic plastics.

Rubber comes in for a good deal of attention. There is a 51-page chapter devoted to "Rubber Adhesives" and a 22-page chapter to "Adhesives for Metal and Rubber". Specific tests for rubber adhesives are discussed in the chapter on "Tests and Specifications for Adhesives". The chapter on "Rubber Adhesives" touches on latex adhesives, the solvent type of rubber cement, cyclized rubber cements, phenol-modified rubber adhesives, oxidation effects on rubber

products, olefin polysulfide cements, synthetic rubber cements, chlorinated and cyclized synthetic rubber cements, etc. Rubber-to-metal assemblies are covered in the chapter on "Adhesives for Metal and Rubber".

There are twenty chapters in all, plus an extensive combination author and subject index. References to authors are printed in the past in comparison with the more colorful and utilitarian in italics for the reader's information. In addition, extensive bibliographical references appear at the end of each of the chapters. [From *The Rubber Age* of New York.]

SYMPOSIUM ON PLASTICIZERS. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y. $7\frac{1}{4} \times 10\frac{1}{4}$ in. 96 pp. \$1.75.—Reproduced from the April, 1947, issue of the *Journal of Polymer Science*, this booklet consists of the seven papers presented at the Symposium on Plasticizers held at the University of Buffalo, June 7 and 8, 1946. The papers, with their authors indicated in parentheses, include the following: Survey of Plasticizers for Vinyl Resins (M. C. Reed); Application of a Mechanistic Theory of Solvent Action to Plasticizers and Plasticization (A. K. Doolittle); Internal Plasticization: The Effect of Chemical Structure (V. L. Simril); Effect of Plasticizers on Second-Order Transition Points of High Polymers (R. F. Boyer and R. S. Spencer); Creep Behavior of Plasticized Vinylite VYNW (W. Aiken, T. Alfrey, Jr., A. Janssen, and H. Mark); Use of Perbenzoic Acid in Analysis of Unsaturated Compounds. I. Preparation and Stability of Solutions of Perbenzoic Acid (I. M. Kolthoff, T. S. Lee, and M. A. Mairs); Use of Perbenzoic Acid in Analysis of Unsaturated Compounds. II. Determination of External Double Bonds in Synthetic Rubbers (I. M. Kolthoff and T. S. Lee). [From *The Rubber Age* of New York.]

MODERN PLASTICS ENCYCLOPEDIA: 1947. Published by the Plastics Catalogue Corp., 122 East 42nd St., New York 17, N. Y. In Three Volumes. 9×12 in. 1,556 pp. Prices: U.S.A., \$8.50; Canada, \$11.00; Foreign, \$12.00.—The latest edition of this comprehensive plastics encyclopedia, the eleventh to be issued, is published for the first time in three volumes. Volume I covers the most recent developments and applications for all types of materials, coatings, films, fibers, fabrics, laminates, and resin-woods, and includes a selected bibliography on German plastics. Volume II is devoted to processing problems of all types, and includes complete directories of the plastics industry, covering names and addresses of material and chemical manufacturers, machinery manufacturers, molders, laminators, etc. Volume III is devoted entirely to ten special charts, including one covering the properties of synthetic rubbers, each chart designed to facilitate reference and handling. The directory section, which is part of Volume II, is available separately for \$1.00, while Volume III, containing the charts, is available separately for \$3.75. [From *The Rubber Age* of New York.]

CHEMISTRY AND TECHNOLOGY OF PLASTICS. By Raymond Nauth. Published by the Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 6×9 in. 522 pp. \$9.50.—Although there are several excellent books available covering the chemistry and technology of plastics, particularly the "Handbook of Plastics" by Simonds and Ellis, the book under review is a welcome addition to the technical literature. It is clear, concise and yet comprehensive. The author has left no stone unturned to acquaint his readers with all types of

plastics, their properties, their characteristics and their applications. Liberal use is made of photographs and charts throughout the book and, in most cases, a list of reading references appears at the end of the various sections.

The book is divided into five chapters, as follows: (1) Thermosetting Resins; (2) Thermoplastic Resins; (3) Cellulose Plastics; (4) Synthetic Rubber, Natural Resins, and Plywood; (5) Mold Design and Equipment. A glossary of common chemical and technical terms used in the plastics industry is included in the Appendix, which also contains a number of valuable tables. The section devoted to the synthetic rubbers includes a chart giving the properties of these rubbers, as well as of a number of so-called pseudo-rubbers. Incidentally, in discussing thermosetting plastics, the author groups such synthetic rubbers as Buna S, Buna N, Neoprene and butyl under the term of "Vulcelastics." A subject index is included. [From *The Rubber Age* of New York.]

PHOTOLYSIS OF RUBBER *

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The increased deterioration in useful physical properties which rubber articles undergo when exposed to light presents a major problem to the rubber industry. Considerable success in combating such deterioration has been achieved by empirical methods, but more rational approaches based on fundamental knowledge of the photochemical processes involved are clearly desirable. The many previous and entirely qualitative investigations into photoinduced changes of rubber and related polymers can be broadly divided into two groups in the following manner: (1) attempts to define the action of light in promoting oxidation and to elucidate the function of antioxidants¹; (2) studies of the gel formation which ensues when rubber solutions denied access to oxygen are irradiated by visible or ultraviolet light². Although the former group deals with the more important natural problem, the latter, by seeking in part to determine the photochemical behavior of the isolated rubber molecule, is concerned with a subject which must be generally understood before conclusions about more complex photoreactions involving other substances, including oxygen, can be finally expressed. Most of the work on photogelation has involved the use of so-called active solvents, *e.g.*, halogenated paraffins, or sensitizers, *e.g.*, ketones, which are certainly more easily dissociated by light than rubber hydrocarbon and whose fragments appear in the resultant gels. While the products may be of some interest to the problem of correlating cross-linking and vulcanization, the experiments are worthless in a mechanistic sense. The potentially more relevant information obtained from saturated hydrocarbon solutions in the absence of sensitizers is, in the main, equally vague for the following reasons: (1) crude, imperfectly purified, or milled rubber was used in which the appreciable nonhydrocarbon content might provide the photoactive centers; (2) insufficient rigor was exercised in eliminating oxygen, which on reaction so effectively leads to oxidative chain scission on the one hand and molecular build-up by interaction of labile oxygenated groups on the other; (3) the occurrence and extent of chemical reaction were judged by purely relative and noncalibratable gelation changes. The object of the present work, therefore, was to see whether highly purified and rigorously isolated rubber hydrocarbon is affected by irradiation, and if so, to investigate the photolysis by a more direct analytical method. Experiment shows that rubber illuminated by a mercury lamp decomposes very slowly with the liberation of a mixture of gases whose rates of formation under varying conditions permit some of the reaction characteristics to be accurately specified.

EXPERIMENTAL

PREPARATION OF SAMPLE

The specimens of rubber employed were either the intermediate fraction³ or were obtained by fractionating acetone-extracted pale crepe from benzene—

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TABLE I
ANALYTICAL AND SPECTROGRAPHIC DATA OF FRACTIONATED RUBBER

Fraction	Nitrogen (%)	Log ϵ at 260 $m\mu$	Fraction	Nitrogen (%)	Log ϵ at 260 $m\mu$
Acetone-extracted crepe	0.29		8	0.02	0.15
Crepe sol	0.30	1.42	9	0.01 ₅	0.27
Crepe gel	0.34		10	0.12	0.92
1	0.60		11	<0.01	-0.30
2	0.14	0.98	12	0.02 ₅	0.29
3	0.03	0.34	13	<0.01	-0.25
4	0.28	1.36	14		
5	0.06	0.45	15	0.01	-0.15
6	0.04	0.72	16	<0.01	-0.30
7	0.08	0.57	17		-0.10

hours, -0.3 after 7 hours, -0.3 after 30 hours). This illustrates the caution with which similar results observed with other than the purest hydrocarbon should be interpreted. Srinivasan⁵, for example, has described comparable absorption changes with relatively impure rubber ($\log \epsilon_{260} = 1.5$), but his explanation in terms of polymerization and depolymerization of the rubber should obviously be accepted with reserve.

PHOTOLYSIS AT ABOUT ROOM TEMPERATURE

The finely cut rubber (2 grams) was contained in a transparent silica tube (1-inch diameter) attached vertically to a simple vacuum line incorporating a trap in series and a McLeod gage; provision was made for removing part of the volatile product for analysis. Evacuation was effected by Hyvac and mercury diffusion pumps. The initial degassing procedure consisted of pumping continuously with a liquid oxygen trap adjacent, first for 25-30 hours at room temperature—the glass being flamed frequently—then with the rubber heated to 100° C in an oil bath for about 20 hours, and finally at room temperature again. A "sticking vacuum" of 1-2 cm. was thus obtained. After every experiment the apparatus was pumped out for a day. The same rubber sample was used in most of the experiments reported and certainly when comparative data were required. The light source was a Hanovia U-shaped S-250 mercury lamp with reflector, normally placed 12 cm. from the rubber, the latter being maintained at constant temperature by immersing its container in a stream of tap water running through a small tank fitted with a clear silica window. The light intensity measurements reported throughout this paper were determined with the uranyl oxalate actinometer⁶, whose upper wave-length limit of efficiency lies beyond the 4358 Å. mercury line which was the present limit for quantitative work. The solution used (0.0025 *M* in uranyl oxalate, 0.0025 *M* in oxalic acid) transmitted appreciably beyond 3126 Å., and the observed intensities at longer wave lengths were corrected in accordance with the emission characteristics of the lamp. On irradiation, the rubber immediately evolved gas at a uniform rate, a typical plot being shown in Figure 1.

Variation in rate of gas formation with light intensity.—Intensity reductions were made by actinometrically calibrated perforated screens. A strictly linear dependence was observed (see Table II).

Quantum yield of gas formation.—0.18 gram of rubber was deposited as a slightly concave film on the rear inside plane face of a silica cell 4 cm. in diameter by slowly evaporating a cyclohexane solution in an atmosphere of nitrogen. After the usual degassing procedure, the rates of gas formation and

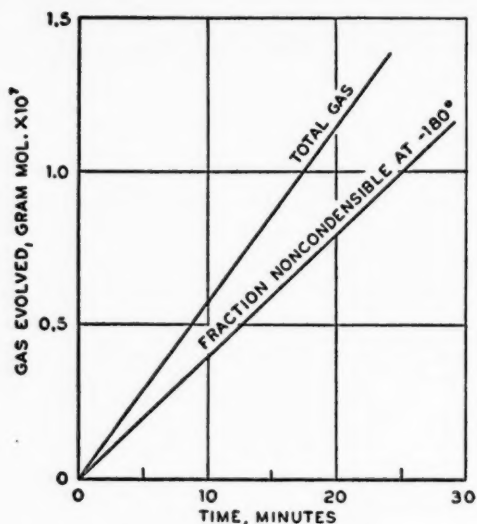


FIG. 1.—Photodecomposition of solid rubber at 14° C.

light absorption were compared for unfiltered radiation, the latter being determined by following the decomposition of uranyl oxalate solution contained in a silica cell of slightly greater diameter placed behind the reaction cell. The usual blank experiment corrects for absorption and scattering by the cell, but scattering by the rubber film has not been allowed for. The rate of formation of noncondensable gas was 4.4×10^{12} molecules per sec.; the rate of light absorption was 1.1×10^{16} quanta per sec.; hence, $\Phi = 4.0 \times 10^{-4}$.

TABLE II
DEPENDENCE OF PERMANENT GAS EVOLUTION ON LIGHT INTENSITY

Relative intensity	Rate of gas formation (gram moles per sec. $\times 10^{15}$)
1.00	9.75
0.10	0.99
0.021	0.22

Variation in rate with wave length of light.—The filters employed were certain of the gaseous and liquid combinations described by Bäckström⁷ or minor modifications of them and, for wave lengths $> 350 \text{ m}\mu$, various glasses made by Chance Bros., Birmingham. In view of the very small decomposition rates, a high degree of monochromatism was not practical, sufficiently high transmission requiring wave bands of at least $40 \text{ m}\mu$. When corrected to uniform intensity, the relative rates observed with the filtered light give a measure of the efficiencies of the decomposition at the various wave lengths, and these are plotted against the mean wave length transmitted by the filter in Figure 2.

Temperature coefficient of noncondensable gas formation.—The rate variation between 70° and 200° C shown in Figure 3 corresponds to an Arrhenius activation energy of 1.5 kcal.

Analysis of gaseous products.—By using an apparatus essentially similar to Langmuir's original arrangement for gas analysis at very low pressures⁸,

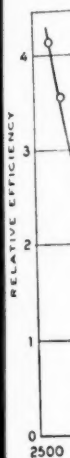


FIG. 2

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portions of the noncondensable gas were passed over copper oxide heated to $300^\circ \pm 5^\circ \text{C}$. The products were condensed in a liquid oxygen trap and then analyzed for carbon dioxide (by expanding at -78°C and measuring the pressure of a known volume in a McLeod gage) and water (by transferring to a small bulb of known volume and then observing the pressure generated at a temperature substantially above the condensation point). Due largely to the very small quantities analyzed ($1-3 \times 10^{-6}$ gram mole), the results were not sufficiently precise to permit detailed description of the components, but certain features are clear. Data averaged from numerous experiments indicate that 1 gram mole of noncondensable gas submitted to combustion over copper oxide yields the following: 0.05 ± 0.03 gram mole of unburnt gas, 0.30 ± 0.05 gram mole of carbon dioxide, and 1.0 ± 0.1 gram mole of water. The quantities of the products relative to the amount of gas analyzed and the high water-carbon dioxide ratio are compatible only with a high hydrogen content. The

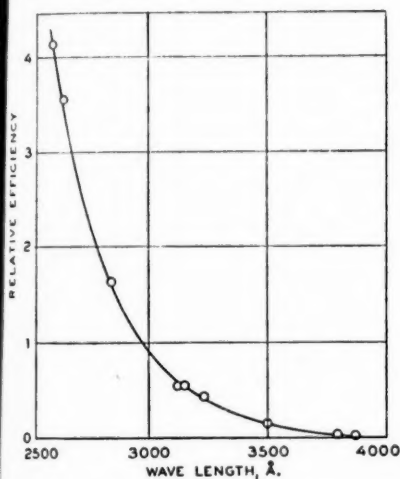


Fig. 2.—Efficiency of the photolysis between 2500 and 4000 Å.

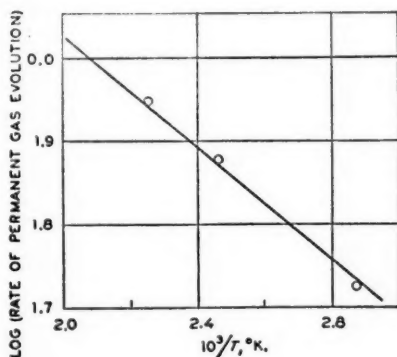


Fig. 3.—Temperature coefficient of permanent gas production.

photolysis of related hydrocarbons yields a complex product mixture including hydrogen and low-molecular hydrocarbons⁹, and the latter are no doubt the main source of the carbon dioxide produced in this case, although the presence of a small quantity of carbon monoxide from any remaining trace of oxygenated material in the rubber cannot be definitely excluded. Methane is practically unaffected over copper oxide below 300°C unless combustion is induced by the burning of other hydrocarbons¹⁰, and therefore is unlikely to be present to the extent of more than a few per cent. A mixture of about 80 per cent hydrogen and about 20 per cent simple hydrocarbons—some only partially combustible under the conditions used—is consistent with the analyses; in view of the doubtful diagnostic value of more precise data in defining the primary dissociation process in a condensed phase the difficult problem of exact analysis was not undertaken. Attempts to analyze the condensable fraction indicated another hydrocarbon mixture of no special feature, which was not examined further.

Examination of rubber.—Distinct physical changes were the rapid insolubilization, *i.e.*, within about 0.5 hour of irradiation, leading to swelling behavior in liquids roughly comparable to that of vulcanized rubber, and a plasticity decrease (Mooney values of 93 before and 125 after about 170 hours of irradiation). Increased molecular complexity by cross-linking is thus evident, but attempts to express this and possible changes in unsaturation quantitatively were frustrated by the absence of measurable changes prior to insolubilization.

PHOTOLYSIS AT HIGHER TEMPERATURES

In these experiments, the rubber (0.5 gram) was placed in a silica tube (0.75-inch diameter) attached horizontally to the vacuum line and surrounded by another silica tube (1.25-inch diameter) which could be heated electrically by widely spaced turns of 18-gage nichrome wire fed from the 12-volt supply. A thin glass, closed tube reaching to within 1 inch of the end of the rubber-containing tube was sealed into the apparatus to serve as a thermocouple

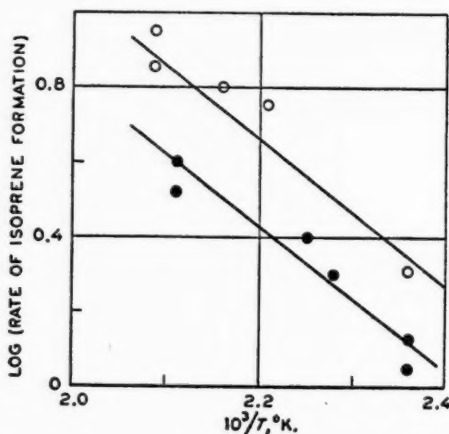


Fig. 4.—Temperature coefficient of isoprene formation.

pocket. The mercury lamp was placed immediately below the silica tubes, the arc being about 6 cm. from the inner tube. The degassing procedure described above was always carried out before investigating the photolysis. On irradiating at temperatures $> 150^\circ C$, very small quantities of isoprene, identified by its vapor pressure-temperature relation and measured by the pressure exerted in a known small volume at about $12^\circ C$, began to appear in the gaseous product. To minimize dimerization of any isoprene formed, pumping was maintained during the irradiation and the condensible products retained in a liquid oxygen trap. Measurement of the rate of isoprene formation was complicated by softening of the rubber and a consequent change in the irradiated surface, particularly at temperatures $> 180^\circ C$, which caused appreciable decreases in rate when several successive experiments were made with one sample. For this reason, and because at temperatures above $200^\circ C$ the thermal degradation assumes predominance, it was necessary to confine measurements to the temperature range 150 – $200^\circ C$, although even at $200^\circ C$ the amounts of isoprene produced were only about 2×10^{-7} gram moles per hour,

and to make rate comparisons from the amounts of isoprene formed in the minimum time required to give a measurable quantity. The individual points in rate *vs.* temperature plots so derived are clearly of limited accuracy, but each series obtained by proceeding from the lowest to the highest temperature in turn allowed a reasonable estimate of the temperature coefficient and thus of the Arrhenius activation energy (10 kcal.) to be made (Figure 4).

DISCUSSION

PHOTOLYSIS PROCESS

The photolysis is notable first for the sharp differentiation which is revealed between the distribution of electronically and thermally acquired energy in the rubber molecule. The primary dissociation in the thermal decomposition of rubber occurs at the single C—C bond midway between the double bonds, the energy required being reduced much below that necessary to sever a normal C—C bond owing to the resonance energy contributed by the allylic fragments produced¹¹. Both parts of the broken chain then tend to split off successive molecules of isoprene or dipentene very readily until some other reaction intervenes to stop this "peeling-off" process. The heat of the peeling-off reaction has been estimated to be about 10 kcal. in the case of isoprene¹², which should be readily liberated at room temperature, therefore, once the initial chain scission has occurred. The extremely small yields of isoprene now measured indicate that this latter condition is not fulfilled in the photolysis to any appreciable extent, although more than the requisite energy is conveyed to the molecule by the absorbed quanta.

The main course of the photolysis seems analogous to that shown by simple related olefins, insofar as results and deductions pertaining to gaseous systems are applicable to a condensed phase. Kieffer and Howe¹³ found that isobutene irradiated at 1900 Å. at pressure up to 60 mm. yielded hydrogen, methane, a hydrocarbon mixture averaging 2.25 carbon atoms per molecule, and a polymer averaging 9.05 carbon atoms per molecule, with respective quantum yields of 0.03, 0.10, 0.16, and 0.45. The experimental data were satisfactorily interpreted by a free-radical reaction mechanism in which excited isobutene molecules, not otherwise deactivated by collision, dissociate in the two obvious alternative ways to give hydrogen atoms or methyl radicals; the radicals formed either react with olefin molecules or recombine in the gas phase or on the walls. At the higher pressures in the range investigated, quenching of the excited by the normal isobutene molecules becomes increasingly important and leads to a diminution in the overall quantum efficiency. In view of the large energy input (about 150 kcal. per gram mole) into a small molecule with relatively readily dissociable bonds adjacent to the ethylenic-absorbing center, it is not surprising that the primary dissociation should be complex. As Kieffer and Howe¹³ recognized qualitatively, quoting H. S. Taylor, allylic resonance energy substantially reduces the energy required to sever the α -methylenic C—H bonds (actually to about 80 kcal. per gram mole); if therefore, the transmission of the intense energy of the excited double bond through the adjacent C—C single bonds is not grossly inefficient, α -methylenic C—H and simple C—C bond scission are of comparable probability under these conditions. In the spectral range of our experiments (>2500 Å.), the primary process is more difficult to assess because of the following reasons: (1) the acquired energy is not greatly in excess of the dissociation energies, and therefore the transmission efficiencies of intervening bonds become critical; and (2) the absorbing system is less

definite. With regard to the latter, Carr and Walker¹⁴ first noted that the absorption curves of monoolefins showed characteristic long-wave (> about 2400 Å.) step-outs whose position and intensity were governed by the degree of alkyl substitution at the double bond. The excitation process responsible for this weak absorption has not yet been identified, but evidently some coupling exists between the alkyl groups and the double bond, and therefore an extended distribution of the absorbed energy. As hydrogen is the main low-molecular product, α -methylenic C—H bonds must be the principal dissociation sites and therefore, since the reaction threshold extends to about 3650 Å., practically the whole of the absorbed energy must occasionally be transferred to the dissociating bonds. The various possibilities of secondary reaction and the fact that reaction leading to nonvolatile products cannot be measured render deductions from our data inconclusive, but it seems true that energy transference in the system $H-C-C=C$ is sometimes very efficient although the usual hyperconjugative interaction is not revealed in ultraviolet spectra¹⁴, and that complete dissociation affords only a minute dispersion route for the absorbed energy, collisional deactivation and Franck-Rabinovitch recombination being highly effective quenching processes in the condensed phase. Since only hydrogen atoms formed within a few atomic diameters of the surface escape to combine on the walls of the containing vessel, most of the molecular hydrogen probably results from the exothermic reaction, $H + RH \rightarrow H_2 + R$, where R is an allylic hydrocarbon radical. Other energetically favored secondary reactions need not be elaborated, except to note that the combination of hydrocarbon radicals or attachment of a hydrocarbon radical at a double bond, both facile reactions, leads to cross-linking polymerization. These views, as well as some experimental features, align closely with those recently discussed by Gunning and Steacie¹⁵ in presenting their data on the mercury-sensitized decomposition of polyene.

APPLICATION TO THEORIES OF PHOTOGELLING

The gelling of pure rubber hydrocarbon dissolved in nonabsorbing solvents on exposure to ultraviolet light can now be definitely attributed to its basic photochemical activity. Since intermolecular C—C bonds create cross-linking, the high stability of gels so formed—except to reagents, *e.g.*, oxygen, inducing severe molecular degradation—and their resistance to peptizing solvents are readily understood. On the other hand, the very small breakdown which rubber thus undergoes implies that when more photoactive substances, *e.g.*, ketones, are present they play the decisive photochemical role, and in practice this is nearly always the case.

ACTIVATION ENERGY OF ISOPRENE FORMATION

In considering the thermal decomposition of rubber in which isoprene and its independently formed dimer, dipentene, are the sole low-molecular products, Bolland and Orr¹² have expressed the observed overall activation energy of isoprene formation, ΔE_i , as a composite quantity given by:

$$\Delta E_i = \Delta E_f + \Delta E_f^i - \Delta E_{Ez}$$

where the terms on the right-hand side of the equation are the activation energies for primary radical formation, for separation of isoprene from a polyisoprene unit terminated by an allyl radical, and for the hydrogen exchange

reaction regarded as the probable chain-stopping process, respectively. Sufficiently good estimates of these quantities can be made to leave no doubt concerning the general correctness of these authors' analysis of the degradation process, but experimental corroboration of the theoretical values employed is necessary to establish certain details. ΔE_f was assumed to be not much greater than the corresponding heat of reaction term, known relatively accurately as 43 kcal.; Evans¹⁶ calculated value (14 kcal.) was assigned to ΔE_f ; and the estimate of Rice and Herzfeld¹⁷ for the exchange of a hydrogen atom between alkyl radicals (20 kcal.) taken for ΔE_{Ez} . In view of the approximations involved, the latter two terms were regarded as roughly equivalent, thereby cancelling each other out. Assessing the ΔE_{Ez} estimate is especially problematical. First, there is the uncertainty in adopting the Rice-Herzfeld figure for hydrogen exchange between allyl radicals, which may well be more energetically facile than that between saturated alkyl radicals. Secondly, various experimental activation energies for the latter process¹⁸, although dependent on the interpretations of the reaction mechanisms and on the energies assigned to C—C and C—H bonds, are consistently less than 20 kcal., in some cases being as low as 4–8 kcal. A value of 10–15 kcal. would seem to be nearer the truth, and since the activation energy for the photoproduction of isoprene is equal to $\Delta E_f - \Delta E_{Ez}$, ΔE_f thus equals 20–25 kcal. Within accuracy limits this is in reasonable agreement with the theoretical estimate, which Bolland and Orr¹² considered on other grounds as possibly 5–6 kcal. too low.

SUMMARY

Rubber hydrocarbon irradiated *in vacuo* is decomposed by ultraviolet light of wave length less than 4000 Å. The rubber very rapidly becomes insoluble, and liberates a gaseous mixture which consists mainly of hydrogen when the irradiation temperature is less than 150° C. The reaction characteristics have been investigated, and point to the occurrence of dissociation processes similar to those deduced for comparable simple olefins. When irradiated above 150° C, small but significant amounts of isoprene appear in the volatile product, thereby providing an experimental means of determining the activation energy for the separation of isoprene from a polyisoprene chain terminated by an allyl radical.

ACKNOWLEDGMENT

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CHAIN STRUCTURE OF VINYL AND DIENE POLYMERS IN RELATION TO POLYMERIZATION MECHANISM *

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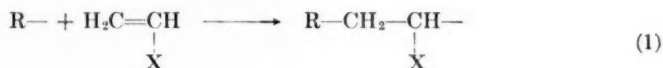
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The structural units of vinyl polymers generally occur in a regular head-to-tail sequence¹ ($-\text{CH}_2\text{CHCH}_2\text{CH}-$) such that the substituent occurs on alter-



nate atoms of the chain. Good evidence for this type of structure has been found for polystyrene², polyvinyl acetate³ (i.e., polyvinyl alcohol resulting from the hydrolysis of polymerized vinyl acetate), the polymer of methylvinyl ketone⁴, the polymer of methylisopropenyl ketone⁵, and polyvinyl chloride⁶. Polymers of disubstituted ethylenes, such as isobutylene⁷ and vinylidene chloride⁸, also possess the head-to-tail structure. Marvel and Cowan⁹ concluded that α -haloacrylates polymerize to give some, at least, of the head-to-head, tail-to-tail structure, although the evidence in this instance may be open to question.

The prevalence of the head-to-tail arrangement is easily explained in terms of the free-radical mechanism of chain growth. The free radical may add in either of two ways to the monomer:



where X is a substituent atom or group, e.g., $-\text{OCOCH}_3$, $-\text{C}_6\text{H}_5$, $-\text{Cl}$ etc. If either addition step occurs successively to the virtual exclusion of the other, a head-to-tail polymer is produced. Thus, it is inferred from structural evidence that one of them supersedes the other. The free radical produced in reaction (1) is generally stabilized by the presence of the substituent on the free-radical carbon atom. No such stabilization occurs in the product of reaction (2). It does not necessarily follow that the product of lowest energy is the one formed most rapidly. However, in reactions such as these, where the activation step involves primarily a shift of electrons with only minor (and similar) changes in bond dimensions, a greater rate of formation of the product of lower energy may safely be predicted. On this basis, reaction (1) is concluded to be the one which occurs preferentially.

While the above considerations provide a logical explanation for the observed predominance of the head-to-tail structure, they also lead to the expectation that a minor percentage of the head-to-head, tail-to-tail structure should also occur, particularly in those instances where resonance stabilization of the free radical by the substituent is small, e.g., when $\text{X} = -\text{Cl}$ or $-\text{OCOCH}_3$.

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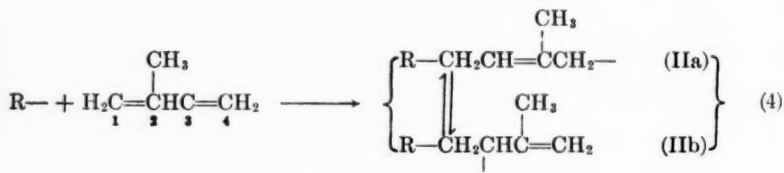
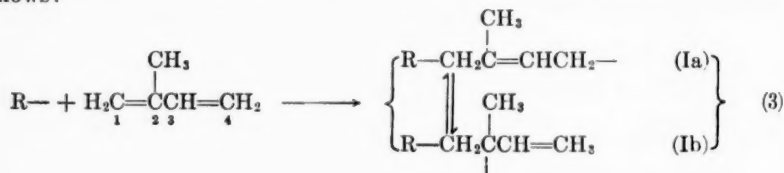
In other words, the stabilizing effect of the substituent(s) should not, in all cases at any rate, be so great as to suppress the competitive reaction (2) to the extent that it can be neglected entirely. Marvel and Denoon³ found that the reaction of periodate with polyvinyl alcohol prepared from polymerized vinyl acetate was not perceptible by chemical determination of residual periodate. Their procedure probably would have detected a proportion of 1,2-glycol structure in excess of about two per cent of the total number of units.

Experiments carried out some time ago in this laboratory by Leutner¹⁰ furnish positive evidence for structural arrangements in polyvinyl alcohol which are subject to splitting by reagents known to attack 1,2-glycols. When an aqueous solution of high molecular weight polyvinyl alcohol is treated with periodic acid, sodium periodate, or lead tetracetate, there is an immediate decrease in viscosity. The change is so marked as to be easily demonstrable without recourse to quantitative measurements¹¹. Estimates of molecular weight based on intrinsic viscosity measurements indicate a final degree of polymerization of about 100. (This figure represents a tentative result which may require revision on the basis of further work now in progress.) This result shows that reaction (2), whereby 1,2-glycol diacetate structures are produced, occurs at about 1 per cent of the rate of reaction (1) under specified conditions of polymerization. About 2 per cent of the hydroxyl groups in the polyvinyl alcohol occur in 1,2-glycol structures, which is approximately the limit of sensitivity of the chemical determination method employed by Marvel and Denoon³.

Diene polymers afford further evidence for oriented addition¹². Thus, Harries¹ found that the products of hydrolytic cleavage of the ozonide of thermally polymerized isoprene were similar to those from natural rubber, and gutta-percha, *i.e.*, a high yield of levulinic aldehyde and acid was obtained. Only very small percentages of succinaldehyde and acid and of acetylacetone could be isolated¹⁴. These results lead to the conclusion that polyisoprene (when formed by a free-radical propagation step, *i.e.*, excluding sodium polymerization) consists of a preponderance of 1,4 units, and, further, that these are arranged in head-to-tail sequences as follows:



Free-radical addition may occur either at carbon atoms 1 or 4 of isoprene as follows:



In each case a resonance hybrid is formed, and the ultimate configuration of the unit in question is determined by the next addition of monomer. (Addition at carbon atoms 2 and 3 is extremely unlikely, owing to the absence of a resonating structure for the resulting adducts, which would therefore possess considerably higher energies than those indicated above.) If it takes place, for example, at carbon number 4 of the hybrid of reaction (3), the monomer in question occurs in the polymer as a 1,4 unit; if addition takes place at carbon number 2, it becomes a 1,2 unit¹⁵. The preponderance of 1,4 units arranged in head-to-tail sequence in thermally polymerized isoprene demonstrates that one of the reactions (3) or (4) occurs in marked preference to the other. In other words, the rates of addition at carbon atoms 1 and 4 must differ considerably. The ozonolysis results offer no clue as to which of these reactions is the preferred one.

In vinyl polymerizations a decision between the analogous addition steps (1) and (2) is not possible on the basis of structural evidence alone, although, as pointed out above, knowledge of the influence of substituents on the stability of free radicals leaves little doubt that reaction (1) represents the principal propagation step. In polymers from unsymmetrical dienes, such as isoprene, it is possible to derive information bearing on this problem from an examination of the structures of those units, present in minority, which are not in the 1,4 configuration. Addition according to reaction (3) followed by subsequent reaction in the form (Ib) introduces a 1,2 unit having a vinyl substituent. Hence, detection of vinyl groups in the polymer would constitute proof of the occurrence of addition according to reaction (3). Similarly, detection of isopropenyl groups, which characterize the 3,4 unit formed from radical (IIb), would prove that addition occurs according to reaction (4).

Such evidence does not lead to an unequivocal decision concerning the principal steps by which head-to-tail 1,4 units are formed. The adduct formed by the infrequently occurring addition step conceivably might prefer to react in the "b" form, *i.e.*, as (Ib) or (IIb) as the case may be. The structure of the abnormal units, *i.e.*, those units which are not 1,4, would then not be indicative of the main addition step. On the other hand, it is reasonable to postulate that the relative rates of reaction in the (Ia) as compared to the (Ib) forms would not differ in order of magnitude from the relative rates for the (IIa) as compared to the (IIb) forms. Detection of 1,2 or of 1,4 units should at least afford presumptive evidence on whether (3) or (4) represents the preferred addition step.

Field, Woodford, and Gehman¹⁶ have shown recently that the infrared spectrum of emulsion-polymerized isoprene includes, in addition to bands characteristic of the predominant 1,4 structure, other weaker bands near 1000 cm^{-1} and 914 cm^{-1} which are indicative of the vinyl group corresponding to 1,2 addition. Other bands occur near 880 cm^{-1} , which might arise from isopropenyl groups representing 3,4 units, although this interpretation is open to question; these bands may have an entirely different origin¹⁷. At any rate, the presence of a minority of 1,2 units, accompanying the preponderance of 1,4 units, seems well established by the infrared spectra. This result, according to the arguments presented above, supports reaction (3) as the preferred addition step in free-radical polymerization of isoprene. Further information on the structure of polyisoprene is needed before a definite decision can be reached, however. A consideration of the stabilizing influence of the methyl substituent on the free-radical structure occurring in (Ib) above leads to the prediction that addition according to (3) should occur in preference to (4).

To recapitulate, ozone degradation studies establish the occurrence of oriented addition of isoprene, but they fail to distinguish which orientation is

the preferred one. It should be possible from further structural studies, for example, by infrared spectroscopy, to differentiate between the two conceivable addition steps. Available evidence favors reaction (3).

Isoprene polymerized with sodium as the catalyst contains very little head-to-tail 1,4 structure, according to the results of ozone degradation¹³. Infrared spectra¹⁶ show further that 1,4 units, regardless of orientation, are present in minority. An abundance of 3,4 units with a possible minor proportion of 1,2 units is indicated by the infrared spectra¹⁶. In sodium polymerization the active terminus of the growing molecule is believed to be a carbanion. Evidently in this type of polymerization the growth process corresponding to reaction (4), in which the free radical is to be replaced by a carbanion, is preferred. Furthermore, the resonating ion reacts preferentially in the form corresponding to form (IIb).

When polychloroprene is subjected either to oxidation¹⁸ or to ozone degradation¹⁹, succinic acid is the principal product. In the latter case, yields of succinic acid as high as 90 per cent were obtained¹⁹, indicating that at least 95 per cent of the units occur in the 1,4 configuration. These methods do not distinguish head-to-tail from head-to-head (or from random) arrangements of the 1,4 units, owing to loss of the halogen substituent during hydrolytic cleavage. The fact that polychloroprene crystallizes when cooled or stretched shows that the structure must be regular for the most part. Hence, a head-to-tail structure is probable¹⁸. As in the polymerization of isoprene, oriented addition of chloroprene is indicated.

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STRESS-OPTICAL PROPERTIES OF RUBBER *

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Considerable progress in the quantitative description of the mechanical properties of rubber has taken place in recent years by the consideration of a rubber as a network of statistically kinked long-chain molecules. A treatment of the optical properties of strained rubber on this basis, with the assumption that the links of the molecular chain are themselves optically anisotropic, has been developed by Kuhn and Gr \ddot{u} n¹ for the special case of simple elongation, and by me² for general homogeneous strain. In the latter case, the rubber has three principal refractive indices, n_1 , n_2 , and n_3 , corresponding to the three principal axes of the strain ellipsoid.

For light propagated along a principal axis, the birefringence is found to be:

$$n_1 - n_2 = C_1 N (\lambda_1^2 - \lambda_2^2) \quad (1)$$

where N is the number of chains per cc. of the network, and λ_1 , λ_2 , λ_3 are the principal extension ratios. The stresses t_1 , t_2 and t_3 are related to the principal extensions by equations of the type:

$$t_1 - t_2 = NkT(\lambda_1^2 - \lambda_2^2) \quad (2)$$

Hence the birefringence in a principal plane is proportional to the difference of the principal stresses, and to the difference of the squares of the principal extension ratios.

By stretching a rubber sheet in two perpendicular directions in such a way as to reduce a homogeneous strain, it has been possible to test these theoretical predictions. The closest agreement was obtained when the rubber was swollen with a solvent. Figure 1, which refers to a pure-gum natural rubber swollen in paraffin to about twice its original volume, confirms Equations (1) and (2) fairly precisely.

In these experiments the stress (t_3) normal to the sheet was zero. In this case, the stress t_1 in the direction corresponding to λ_1 is, according to the theory:

$$t_1 = NkT(\lambda_1^2 - \lambda_3^2) \quad (2a)$$

where λ_3 is the extension ratio in the direction normal to the surface of the sheet. However, on plotting t_1 against $(y_1^2 - y_3^2)$, the points fall, not on a straight line, but on a series of arrays (Figure 2). In any one of these arrays one force f_1 (corresponding to the stress t_1) is constant, while the other force f_2 varies.

A physical explanation of this departure from the behavior predicted by the molecular theory has not been found. It is, however, exactly the type of behavior to be expected from the more general theory of elasticity developed by Mooney³, on the assumption that Hooke's Law is obeyed in shear. From Mooney's theory, the principal stresses are found to be related to the extension

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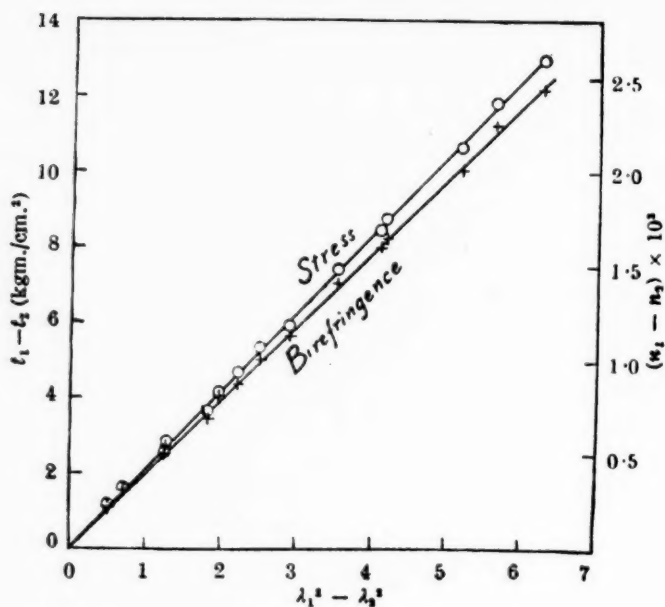


FIG. 1.—Dependence of difference of principal stresses and birefringence on difference of squares of principal extension ratios.

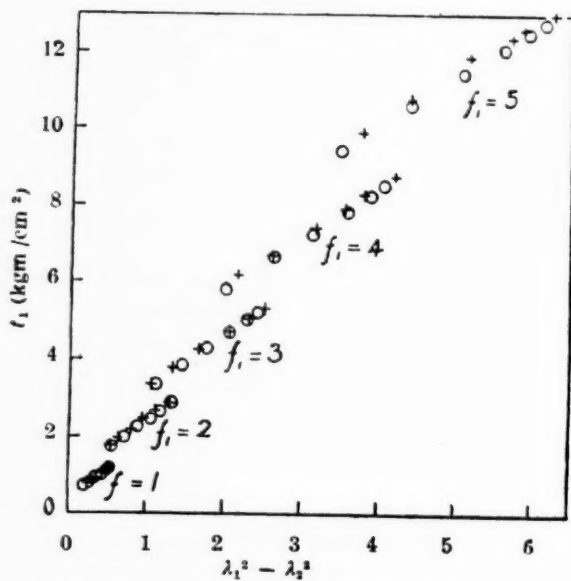


FIG. 2.—Crosses, experimental results; circles, calculated from Mooney's theory, with $G = 2.0$, $K = 0.2$.

ratios by equations of the type:

$$t_1 - t_3 = (G + K\lambda_2^2)(\lambda_1^2 - \lambda_3^2) \quad (3)$$

With a suitable choice of the constants G and K , the graphical solution of these equations leads to results which, when plotted as in Figure 2, agree remarkably well with the experimental data.

For the dry rubber, on the other hand, Hooke's Law was not obeyed in shear, and neither the molecular theory nor Mooney's theory accounted quantitatively for the experimental data, though Mooney's theory provided the closer approximation.

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HIGH-FREQUENCY AND LOW-FREQUENCY SPECTRA AND THE STRUCTURE OF RUBBER *

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Under the influence of an alternating electric field, the loss angle and dielectric constant of a sheet of rubber vary as a function of the frequency, while the conductivity remains negligible even at low frequencies. The essential difference between this behavior and that of the crystalloid liquids already studied by the authors is that, instead of a single absorption curve and a single dispersion curve extending through a narrow range of frequencies, there is a series of curves extending a considerable distance toward the low frequencies. However, the relations between absorption and dispersion remain the same as with crystalloid liquids, so here too the losses can be explained by the orientation polarization, and the same qualitative scheme of dipolar oscillators which follows, with a certain dephasing, the alternations of the field. However, instead of being a single type and individually identical, these oscillators are in

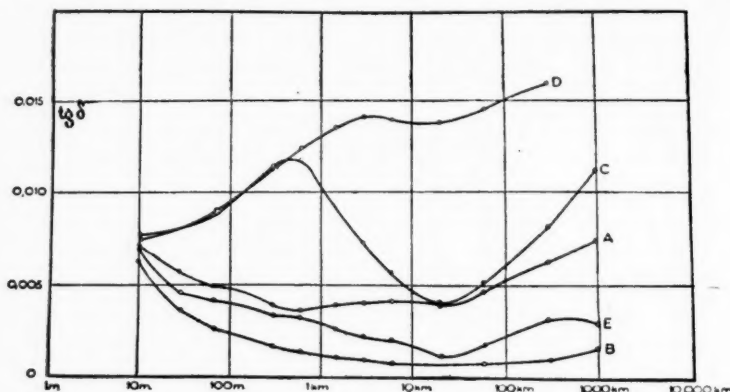


Fig. 1.

this case polyisoprene chains which differ in length and consequently in their relaxation times. This variety of dipoles is evident in the many successive curves. (To develop the spectrum, the authors used chiefly absorption curves.) These curves differ in their positions on the abscissa as a function of the dimensions of the dipoles, and by their height as a function of their concentration and form. When for a group of dipoles characterized by a mean relaxation time, the lengths of the chains and the relaxation times vary progressively from one dipole to another, then the resultants of the different absorption curves representing the different dipoles unite into a single flat extended curve. On the contrary, a group of homogeneous dipoles which are identical or almost identical is represented by a single bell-shaped curve.

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Figure 1 shows the loss angles as a function of the wave lengths (logarithmic scale) of five unvulcanized rubbers which differ in mechanical and dielectric properties. With these five samples, condensers of different capacities to conform to the range of λ values desired were constructed.

Samples A, B and E showed tensile strengths of approximately 180 kg. per sq. cm., and had good dielectric properties. Sample C on the contrary had poor dielectric properties, and its tensile strength was low, viz., 80 kg. per sq. cm. Sample D likewise had poor dielectric properties, but its tensile strength was as high as 230 kg. per sq. cm. In conformity with these properties, it can be seen that the spectra of A, B and E are similar and are characterized, particularly the spectrum of B, by a distribution, with a continuous variation, of chain lengths and of relaxation times around a mean value. On the contrary, the spectra of C and D differ from the spectra of A, B, and E and also differ among themselves. With C, the chain lengths divide themselves into two homogeneous distinctive groups, a group of short chains toward the region of short λ values, and a group of long chains toward the region of high λ values. The mean relaxation times of the two groups differ considerably.

Sample D has the dual characteristic of showing a high concentration of rather long and very long chains and a continuous variation in the lengths of the chains. Both a change in temperature and in vulcanization change considerably the spectrum of rubber. Figure 2 shows, by way of example, the

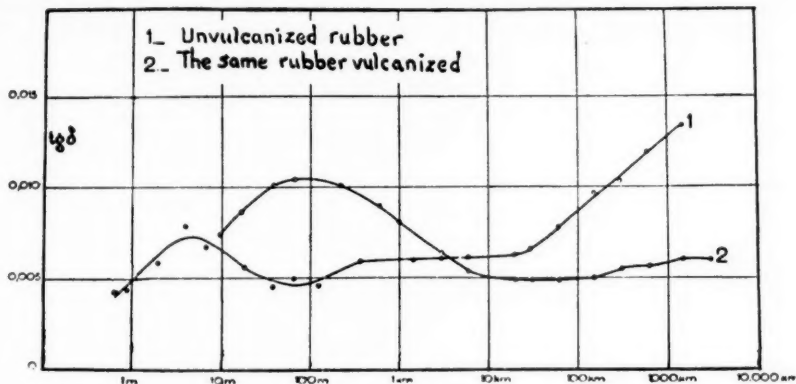


Fig. 2.

effect of vulcanization. The whole spectrum is displaced toward high λ values (an increase in the coefficient of friction). The introduction, with the formation of sulfur bridges, of a supplementary permanent moment (1.58 Debye) affects differently the right part and the left part of the spectrum. It may be assumed that, at the right, the long polyisoprene chains united by sulfur bridges constitute a sort of network. The vibratory movements of the dipoles in the alternating field are greatly obstructed; hence the relatively small losses in spite of the addition of a supplementary permanent moment.

At the left, the short polyisoprene chains which have fixed sulfur would form free dipoles not united with one another. The oscillation in the alternating field would not be disturbed. The addition of a supplementary permanent moment increases the losses.

It is evident, then, that the absorption spectrum of rubber indicates a characteristic pattern of its mechanical and dielectric properties.

THE DEPOLARIZATION OF LIGHT SCATTERED IN SOLUTIONS OF RUBBER LIKE POLYMERS *

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Investigation of the depolarization of light, Δ , scattered by colloidal solutions is one of the methods of determining the dimensions, shape and optical properties of the particles suspended in them.

A study of the state of polarization of the scattered light is found to be especially helpful in this respect. If the incident beam is directed along the x -axis of a rectangular system of coördinates and observation is carried out along the y -axis, the degree of depolarization of the scattered light is usually determined by the ratio $\Delta = I_z/I_x$, where I_x and I_z are the x - and z -components, respectively, of the scattered light. Here one should discriminate between the quantity Δ_v (the electrical vector of the incident light parallel to the z -axis) and the quantity Δ_h (the electrical vector of the incident light parallel to the y -axis).

On the basis of theories advanced by Rayleigh¹, Mie², and Gans³ one may draw the following general conclusions regarding the relation between Δ and the properties of the dispersed phase.

For spherical optically isotropic particles, irrespective of their dimensions, $\Delta_v = 0$. If the particles are anisotropic in shape or in their optical properties, $1 > \Delta_v > 0$.

In a system which does not contain large particles, *e.g.*, for all molecular liquids, $\Delta_h = 1$, irrespective of their anisotropy and shape. On the other hand, when the dispersoid is comparable in dimensions with the wave length of the incident light, $\Delta_h > 1$.

It was found by Krishnan⁴ that $\Delta_h > 1$ for binary liquid mixtures as well as colloid systems, which he interpreted as proof of the existence in the former of large molecular swarms (the Krishnan effect). To explain this effect Gans⁵ proposed a theory in which he assumed that the fluctuations in the density and anisotropy of the various volume elements are correlated, and that the linear dimensions of a swarm are small in comparison with the wave length of the light. Gans arrives at the conclusion that the Krishnan effect ($\Delta_h \neq 1$) may exist only for the case of a nonspherical swarm, whereas for spherical particles, regardless of their optical anisotropy, $\Delta_h = 1$. In the particular case of rod-like particles of length l :

$$\Delta_h = 1 - \frac{4\pi^2}{42} \left(\frac{l}{\lambda} \right)^2 \left[1 - 3 \frac{(g_1 - g_2)^2}{(g_1 - g_2)^2 + (g_2 - g_3)^2 + (g_1 - g_3)^2} \right] \quad (1)$$

where g_1 , g_2 and g_3 are quantities proportional to the difference between the dielectric constants of the medium and the particle along its three mutually perpendicular axes (g_3 in the direction of the long axis of a rod).

* Reprinted from the *Comptes Rendus de l'Académie des Sciences de l'URSS*, Vol. 47, No. 8, pages 550-553, 1945.

By making the plausible assumption for a rodlike particle that $g_1 = g_2 \neq g_3$, Gans obtained:

$$\Delta_h = 1 - \frac{4\pi^2}{42} \left(\frac{l}{\lambda} \right)^2 < 1 \quad (2)$$

However, since for all systems that had been investigated until then experiments gave $\Delta_h \geq 1$, Vrkljan and Katalinić corrected Gans' results and, assuming that a threadlike particle possesses highly improbable optical properties ($g_1 \neq g_2 = g_3$), obtained with the aid of (1) $\Delta_h > 1$. Gehman and Field⁷ were apparently the first to observe the scattering in which $\Delta_h < 1$, while studying solutions of natural rubber.

Since in natural rubber a considerable quantity of colloidal admixtures is always present which may greatly distort the experimental results, we employed solutions of some synthetic polymers to study the depolarization of the scattered light, paying attention to the degree of purity of the solution. The following polymers were investigated: technical natural rubber (smoked sheet), polystyrene, butadiene polymers, and isobutylene polymers (Oppanol and Vistanex).

Polystyrene was obtained by polymerizing monostyrene that had been distilled in a closed vessel and did not contain any noticeable quantity of scattering admixtures. The solutions of polystyrene, as well as those of Oppanol and Vistanex, were purified simply by letting them stand for several days so that any admixture might settle. The absence of any noticeable quantity of colloidal admixture was established by a control measurement of their electrical double refraction. The Kerr effect in the field $E = 40,000$ volts per cm. did not exceed noticeably that for the pure solvent (carbon tetrachloride).

The butadiene rubbers were fractions (of different molecular weight μ) of one and the same polymer, specially prepared and containing the least possible amount of impurities. Their solutions were purified by centrifuging. Natural rubber was found to contain the most colloidal admixtures. Its solution could not be purified by ordinary centrifuging, and we had to resort to a method that we employed elsewhere⁸—multiple action of a strong electrical field, with subsequent centrifuging. This enabled us to prepare clear solutions containing a highly insignificant amount of foreign particles. The presence of the latter was established from the birefringence of the solution in an electric field. Table 1 shows the observed values of birefringence Δn in an electric

TABLE 1
DEPENDENCE OF THE ELECTRIC BIREFRINGENCE OF A SOLUTION OF RUBBER
IN CARBON TETRACHLORIDE ON THE DEGREE OF PURIFICATION

Unpurified solution		Solution after purification by applying a field of 40,000 volts per cm. for a period of 3 hours and centrifuging for 2 hours	
E (volts per cm.)	$\Delta n \times 10^5$	E (volts per cm.)	$\Delta n \times 10^5$
3,600	1.8	9,000	~ 0
6,600	1.8	18,000	0.09
9,600	1.7	25,500	0.24
14,100	2.7	30,000	0.33
18,900	3.6	34,200	0.49
37,500	6.5	39,000	0.68

field E for a solution of natural rubber in carbon tetrachloride. We see that after the solution is acted upon by the electric field for three hours and then

centrifuged, the electro-optical effect decreases tenfold, although it is still several times the value of the Kerr effect for pure carbon tetrachloride.

The degree of depolarization of the scattered light was determined in the usual way, employing Wollastone's prism and an analyzer on the limb⁹. The results obtained are presented in Table 2. As the data show, the solutions of

TABLE 2
DEGREE OF DEPOLARIZATION OF LIGHT SCATTERED IN
SOLUTIONS OF VARIOUS POLYMERS

Polymer, solvent, concentration (by volume)	Degree of purification	Δ_v	Δ_h
Natural rubber—carbon tetrachloride, $c_v = 0.8\%$	Unpurified	0.020	0.51
	Purified by applying a field for 3 hrs. and centrifuging for 2 hrs.	0.015	0.27
Butadiene synthetic rubber—ether, $c_v = 2\%$	Fraction 1; $\mu = 22,000$		
	Before centrifuging	0.032	1.22
	After centrifuging	0.025	0.33
	Fraction 2; $\mu = 40,000$		
	Before centrifuging	0.028	0.93
	After centrifuging	0.022	0.31
Polystyrene—dichloroethane, $c_v = 2.5\%$	After settling for several days	0.049	0.49
		0.037	0.69
Polystyrene—carbon tetrachloride, $c_v = 2.5\%$	After settling for several days	0.016	0.40
Vistanex pentane, $c_v = 0.8\%$; $\mu = 55,000$	After settling for several days	0.022	0.30
Oppanol—pentane, $c_v = 0.8\%$; $\mu = 150,000$	After settling for several days	0.015	0.17

all the polymers are characterized by an insignificant value of Δ_v , and an anomalous depolarization $\Delta_h < 1$.

The degree of depolarization of the scattered light depends on the purity of the solutions. The value of Δ_v decreases somewhat with purification, but the presence of foreign (coarse) particles in the solution especially affects the value of Δ_h ; the purer is the solution, the greater does Δ_h differ from unity. In a number of cases, where the solution contained a great number of colloidal admixtures, we even obtained $\Delta_h < 1$ (e.g., fraction 1 of the butadiene polymer before centrifuging).

Thus, depolarization $\Delta_h < 1$ cannot be regarded as a chance phenomenon due to accidental causes, but is evidently a property that is general for solutions of all rubberlike polymers, and which is the more pronounced, the purer the solution with respect to coarse admixtures.

It is not surprising that such a state of polarization had not been observed in any colloidal system investigated heretofore, for the properties that the scattering particles should possess according to Gans' theory—a considerable elongation in shape, dimensions smaller than the wave length of the light, and negligible optical anisotropy—are the characteristic properties of chainlike molecules in solution¹⁰, and are much more seldom met with together in other colloidal systems.

It is our opinion that the phenomenon considered by Gans in his theory, and experimentally discovered by Gehman and Field and by us, differs in principle from the Krishnan effect, since the basic condition for the origination of the latter ($\Delta_h < 1$) is coarse dispersity of the dispersion medium (the dimensions of

the particles are comparable with the wave length of the light), while the effect described in the present paper is connected with the asymmetry of the particle shape. Therefore it should be properly named the Gans effect.

A study of the Gans effect in solutions of high-molecular compounds is of undoubted interest, since it promises to furnish direct data on the length of the molecular chain in them. However, the results presented in Table 2 show that in a quantitative interpretation of the experimental data one should be cautious, paying serious attention to the purity of the solution investigated.

Here we shall apply the theory only to solutions of polyisobutylenes, since they are the purest with respect to colloidal admixtures, and the Gans effect for them is particularly great. The latter circumstance is quite characteristic, since polyisobutylenes differ from other polymers by the absence of branching in the molecule, which is quite elongated, very much like a rod.

The length of a scattering particle in the solution may be determined with the aid of Equation (2). Inserting $\Delta_h = 0.30$ for Vistanex and $\Delta_h = 0.17$ for Oppanol, we get $l = 4.2 \cdot 10^{-5}$ and $l = 4.6 \cdot 10^{-5}$, respectively. The results obtained for the dimensions of a scattering cell are too large for one molecule. It is possible that, in stationary solution after settling, the molecular chains interlace forming micelles which are considerably lower than an individual molecule.

The solutions of all the polymers are characterized by a small degree of depolarization Δ_v (from 1 to 5 per cent). This signifies that the optical anisotropy of their molecules in the solution is negligible. This conclusion is in good agreement with the results of an investigation of the birefringence of solutions while in flow¹⁰ and in a magnetic field¹¹, and also with the theoretical computation of Kuhn¹².

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A STUDY OF THE STRUCTURE OF BUTADIENE POLYMERS BY MEANS OF OZONOLYSIS *

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One of the factors which determine the intramolecular homogeneity of butadiene-type synthetic rubber is the extent to which the diene enters the polymer by 1,4-polymerization *vs.* 1,2-addition. Another factor involves the arrangement of the two (or more) comonomers throughout the polymer chain; *i.e.*, whether there is a tendency toward bunching of one monomer unit or random alternation of the components within the molecule.

Much has been postulated about the correlation of the factors, particularly the first, with the rubberlike properties of the copolymers. It has been thought that the greater the regularity of the molecule through 1,4-polymerization of the butadiene, all other variables being unchanged, the more desirable would be the properties of the rubber. To test this supposition and to discover some of the features of the monomer distribution, an attempt has been made to degrade the butadiene-styrene copolymer by scission at the double bonds through ozonolysis.

This approach is by no means new. Harries¹ was the first to describe the method; Pummerer, Ebermayer and Gerlach² and Pummerer and Richtzenhain³ have applied it to natural rubber; Alekseeva and Belitskaya⁴ to a 1,1-butadiene-styrene copolymer; Hill, Lewis and Simonsen⁵ to polybutadiene and to a butadiene-methyl methacrylate copolymer; Alekseeva⁶ to a copolymer of butadiene and acrylonitrile and a mixed polymer of butadiene and methacrylonitrile; and Klebanski and Vasil'eva⁷ to polychloroprene. The present findings for the GR-S copolymer are similar to those of Alekseeva and Belitskaya⁴ in regard to the nature of the products identified in the determination of total structure, although the butadiene-styrene ratio of 75-25 changes not only the proportions but also the nature of these products to some extent.

The diagram illustrates the fragments which might be expected from an oxidative ozonolysis of a portion of the GR-S molecule in which are found several of the many possible random arrangements. Each vinyl group from 1,2-polymerization of a butadiene molecule gives rise to a molecule of formic acid, and this should be the only volatile acid which appears in measurable quantities, provided there is no oxidative degradation beyond the expected cleavage of the double bonds. Isolation and identification of the di- and polycarboxylic acids would complete the picture of the structure of the copolymer. Thus, where one 1,2-butadiene unit occurs between two 1,4-butadiene units (portion A), ozonization should produce butane-1,2,4-tricarboxylic acid; when a styrene

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unit occurs between two 1,4-butadiene units (portion B), β -phenyladipic acid should be formed; two contiguous 1,4-butadiene units (portion C) should lead to succinic acid; a portion (such as D) containing several adjacent 1,2-butadiene units should give a polybasic acid; alternation of styrene and 1,2-butadiene units (portion E) should lead to polybasic acids carrying phenyl groups as substituents. Obviously, the piling up of many 1,2-butadiene units and(or) styrene units leads to acids of very complicated structures.

In the present study two samples of GR-S, one standard, G-1 (0.3 per cent modifier), and one insoluble G-23 (under-modified 0.15 per cent modifier), have been ozonized in quantities sufficient to make possible the isolation and identification of several of the di- and polybasic acids. In addition, the amount of formic acid produced by ozonization has been determined on a number of GR-S and related polymers.

STRUCTURE DETERMINATION

The ozone degradation procedure employed by Alekseeva and Belitskaya⁴ for the examination of the structure of a bulk copolymer containing equal amounts of butadiene and styrene was followed, with some modifications, in the present investigation of GR-S. After ozonization and oxidative cleavage of the ozonide, the resulting acids were separated into volatile, water-soluble and water-insoluble fractions. Each portion was examined separately. The volatile acids were titrated with standard alkali and the acidity calculated as formic acid. In Table I are shown the quantities of formic acid obtained from

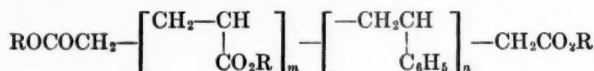
TABLE I
VOLATILE ACIDS FROM OZONIZATION

	G-1	G-23
Formic acid for 100 g. of rubber (g.)	19.5	16.8
Butadiene equivalent (g.)	23.0	19.8
Percentage of butadiene accounted for, assuming the rubber is 77% butadiene	29.9	25.7

100 grams of each of the samples studied, together with the percentages of butadiene accounted for in this manner. The values do not indicate any significant difference between samples G-1 and G-23.

Succinic acid was separated from the water-soluble acids by fractional crystallization. Then the remaining water-soluble acids were converted to their methyl esters, and the esters were subjected to distillation under reduced pressure. Table II shows the amounts of succinic acid and identified esters obtained from 100 grams of each of samples of G-1 and G-23, together with the amounts of butadiene and styrene accounted for.

From reference to the diagram, it is seen that, for the polymer chain to be cleaved by ozone, there must be present a butadiene molecule which has entered by 1,4-addition. Thus, the general formula for the esters derived from the cleavage products of a butadiene-styrene copolymer is:



without regard to arrangement of internal units. Then tetramethyl hexane-1, x , y ,6-tetracarboxylate would be represented by the above formula, where $m = 2$ and $n = 0$; and trimethyl x -phenylhexane-1, y ,6-tricarboxylate would be represented by the same formula, where $m = 1$, and $n = 1$. These esters

TABLE II
COMPOUNDS FROM WATER-SOLUBLE ACIDS
Based on 100 grams of extracted rubber samples

Compounds isolated	G-1			G-23		
	Wt. (g.)	Butadiene (g.)	Styrene (%)	Wt. (g.)	Butadiene (g.)	Styrene (%)
1 Succinic acid	37.05	16.93		30.64	14.02	
2 Dimethyl succinate	37.81	14.00		37.85	14.00	
Total acid and ester		30.93	40.2		28.02	36.4
3 Trimethyl butane-1,2,4-tricarboxylate	28.62	13.32	17.3	25.32	11.80	15.3
4 Dimethyl- β -phenyladipate	11.44	2.47	3.2	8.80	1.90	2.5
5 Tetramethyl hexane-1, $\alpha,\beta,\gamma,6$ -tetracarboxylate	6.44	3.28	4.3	6.92	3.53	4.6
6 Trimethyl- α -phenylhexane-1, $\gamma,6$ -tricarboxylate	4.86	1.56	2.0	5.17	1.66	2.2
Total		51.56	67.0		46.91	61.0
						5.26
						22.9

were only partially identified, so that the exact structural formulas are known. Obviously, several isomers are possible in each case. Alekseeva⁶ isolated a hexane tetracarboxylic ester from the degradation of a butadiene-acrylonitrile copolymer, but it was believed that the secondary carboxyl groups were derived from acrylonitrile units. The complete structure of this ester was not determined either.

The water-insoluble acids were converted to their methyl esters, but neither they nor the remainder of the esters of the water-soluble acids could be fractionated or otherwise separated for characterization. Analysis and refractive index measurements of some unidentified distillates, coupled with the knowledge of the identity of certain esters isolated by earlier workers, led to the tentative identification of these small portions as octane pentacarboxylic ester ($m = 3, n = 0$), phenyloctane tetracarboxylic ester ($m = 2, n = 1$), diphenylsuberic ester ($m = 0, n = 2$), and fumaric ester. The latter might have resulted from the dehydration of malic acid which arose from the introduction of a hydroxyl group *alpha* to a double bond of a 1,4-butadiene unit. None of these compounds represented appreciable fractions of the total butadiene units; however, the supposed dimethyl diphenylsuberate was equivalent to 14.5 per cent of the styrene in sample G-1 and 26.2 per cent of that in sample G-23. It is natural to predict that the higher-boiling residues would contain large numbers of benzene rings and correspondingly large fractions of the styrene. It is not surprising, therefore, that much of the styrene was unaccounted for.

The slight differences in the amounts of esters of water-soluble acids obtained from samples G-1 and G-23 are perhaps not significant; however, the larger amounts of water-insoluble acids found in the degradation of G-23 may be an indication of a structural difference in the two rubbers. Whether this fact is a result of, or is coincidental with the difference in the amounts of modifier used cannot be determined from data available.

DETERMINATION OF TERMINAL VINYL GROUPS

In an effort to determine structural differences between butadiene copolymers prepared under varying experimental conditions, a study has been attempted to show the proportions of butadiene which have entered the polymer molecule by 1,2- and 1,4-addition. The determination of the volatile products, formic acid and formaldehyde, from ozonolysis of the terminal vinyl groups should give a measure of the extent of 1,2-addition. Chloroform solutions of the polymers were treated with ozonized oxygen and decomposed by steam distillation. The products of distillation were oxidized by means of alkaline mercuric acetate, according to the method of Reid and Weihe,⁸ to give carbon dioxide (after acidification), which was absorbed and weighed. The results could be made quite reproducible, although not necessarily accurate in the absolute sense. For this reason, the apparent percentage of 1,2-polymerization has been given the less specific title of "ozonization number".

Ozonization numbers for a variety of polymers are listed in Table III. These values are considerably lower than the results reported recently by Yakubchik, Vasil'iev and Zhabina⁹ for the vinyl content of several polybutadienes and copolymers of butadiene and styrene. After we had completed our work, it was found that our analytical procedure did not account for all of the available formaldehyde and formic acid. It would appear that in some cases our ozonization numbers should be increased by almost 70 per cent. The possibility also exists that ozone may have attacked the polymers at linkages

TABLE III
OZONIZATION OF POLYMERS

Sample	Description	Percentage diene	Ozonization no.
...			
G-1	Natural rubber, crepe	100	11.8 9.5 8.6
G-5	GR-S (75/25), 71% conversion	80 ^b	19.3 19.1
RD-29	GR-S (65/35), 81% conversion	81.4 ^c	20.9
UI-111	GR-S, at 110-130°	80 ^b	17.1 18.0
UI-113	GR-S, large amount of cetyl mercaptan modifier	80 ^b	18.7
RA-187	GR-S, ferricyanide initiated	80 ^b	19.1 16.1
UI-115	GR-S, latex treated with OEI (a thiol modifier)	75 ^a	10.1 8.1
...	GR-S, acid-side	75 ^a	13.4 14.3
...	Unmilled standard GR-S	72 ^a	22.2 18.3
RD-27	Same sample, cold-milled for 40 minutes	72	22.6 22.2
WB-407	Polybutadiene, emulsion at 50°	100	19.4 20.7
WB-16	Polybutadiene, emulsion at 110° for 30 minutes	100	12.0 11.8
G-3	Polybutadiene, sodium sand, 10°	100	22.8 22.2
CKG-666P	Polybutadiene, German, sodium catalyst (Buna-115)	100	38.5 42.2
RD-931	Polybutadiene, Russian, sodium catalyst	100	42.8 40.5
UI-121	Butadiene- <i>m</i> -chlorostyrene (75:25)	75 ^c	12.6 11.8
RD-578	Butadiene-vinylpyridine (75:25)	75 ^a	13.9 12.0
UI-123	Butadiene- β -vinyl-naphthalene (75:25)	67.6 ^c	19.5 07.7
...	GR-N	72 ^a	12.3 14.3
...	Neoprene	100	5.8 7.0 3.4

^a As charged.^b Estimated.^c Measured or known.

other than the double bonds, which would lead to abnormal amounts of formaldehyde and formic acid. For these reasons the actual error in the method is unknown and may vary from case to case.

However, since all polymers were treated under comparable conditions, the relationships which have been shown to exist between the different types of butadiene polymers may be of some qualitative importance. If the relative values shown in Table III are representative of the fraction of butadiene which has polymerized in the 1,2-manner, it is evident that few changes in the emulsion system are successful in reducing this type of polymerization.

EXPERIMENTAL

I. STRUCTURE DETERMINATION

A. Sample G-1.—The rubber sample G-1 used in this investigation was made by the United States Rubber Company in Detroit, Michigan. It was prepared by the standard process except that it was coagulated by means of carbon dioxide. Other specifications for this sample were as follows: conversion 71.4 per cent; benzene-insoluble, trace; intrinsic viscosity 1.97.

Sixty grams of shredded G-1 was extracted in four portions of 15 grams each in a Soxhlet extractor for twenty-eight hours. The extraction medium was the toluene-ethanol azeotrope consisting of 20.2 parts of toluene to 47.3 parts of ethanol by volume (b. p. 76.7°). The extracted material was dried in a vacuum desiccator containing calcium chloride and paraffin. After drying to constant weight, each portion weighed 13.7 grams; the total weight of extracted rubber was 54.8 grams. Each 13.7-gram portion was dissolved in 500–600 ml. of dry chloroform, and each solution was divided into four approximately equal parts for ozonization. A stream of oxygen containing about 2 per cent of ozone was passed through each sample for seven to eight hours at a rate of 110–120 cc. per minute. This time was approximately 25 per cent longer than was necessary for a 10 per cent potassium iodide solution to indicate that some ozone was passing unabsorbed through the rubber solution. During the ozonization a small amount of insoluble material precipitated, while the color of the solution changed from brown to yellow. After ozonization each series of four small samples was recombined for subsequent treatment.

The chloroform was removed from the solution of the ozonide under reduced pressure at room temperature. The ozonide remained as a clear, very viscous liquid. It was cleaved by treatment with 300 cc. of 3 per cent hydrogen peroxide for three to four hours. During this treatment the mixture was warmed first on a water-bath, then brought gradually to the temperature of boiling water. Nearly all of the decomposition product went into solution and only a small amount of a waxy, insoluble material remained.

The solution was removed by decantation and the solid washed with a small amount of water. The original solution and washings were combined and subjected to distillation under diminished pressure. The distillation flask was heated in a water-bath at 35–50° and the receiver cooled in an ice-salt mixture. The distillate was made up to a volume of 1000 cc. with distilled water and a 50 cc. aliquot was withdrawn for titration. The volume of alkali required for each of the 13.7 gram samples of rubber was approximately the same. The acidity was calculated as formic acid, and in this way it was found that the 54.8 grams of rubber produced 10.7 grams of formic acid.

The residues from the four distillations were combined and dried to constant weight in a vacuum desiccator. There was obtained 83.5 grams of non-

volatile, water-soluble acids. Fractional crystallization of this mixture of acids yielded 20.3 grams of succinic acid; m. p. 180–182° (uncor.); neut. equiv. 60 (calcd. for $C_4H_6O_4$: 59). The remainder of the water-soluble acids was esterified with methyl alcohol containing about 8 per cent of hydrogen chloride. The reaction mixture was worked up in the usual manner; the unesterified acids were recovered and treated again with methanolic hydrogen chloride. In all, 59 grams of methyl esters were obtained.

The esters were distilled through a Podbielniak-type column (5×455 mm.) at a pressure of 3–5 mm. The distillation was carried out slowly and at a uniform rate; the distillate was collected in portions of 0.5 to 1.0 gram each. The cumulative yield of distillate was plotted against the refractive index, and the fractions were determined from the resulting curve in the usual way. The following table shows the fractions obtained up to a bath temperature of 210°.

TABLE IV

Compounds	Weight (g.)	n_D^{20}
1 Dimethyl succinate	20.73	1.4192
2 Dimethyl fumarate (?)	1.20	
3 Trimethyl butane-1,2,4-tricarboxylate	15.68	1.4446
4 Dimethyl β -phenyladipate	6.27	1.4972
5 Residue	12.0	

Fraction 1 was shown to be dimethyl succinate by its index of refraction (Bruhl¹⁰ reported n_D^{20} 1.4198), its saponification equivalent and by hydrolysis to succinic acid.

Anal. Calcd. for $C_6H_{10}O_4$: sapon. equiv., 73.1. Found: sapon. equiv., 73.2.

Fraction 2, obtained only in a small amount and impure state, is believed to contain dimethyl fumarate. It was unsaturated to bromine in carbon tetrachloride, but the bromine addition compound could not be isolated.

Fraction 3 was identified as trimethyl butane-1,2,4-tricarboxylate.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.90; sapon. equiv., 77.3. Found: C, 52.07; H, 6.91; sapon. equiv., 77.5.

Acid hydrolysis of a portion of this fraction produced a water-soluble, solid acid which crystallized from acetone as beautiful white prisms, m. p. 119–121° (Hill, Lewis and Simonsen⁵ reported the melting point of butane 1,2,4-tricarboxylic acid as 116–120°, Haworth and King¹¹ as 120–121° and Kay and Perkin¹² as 116–118°).

Anal. Calcd. for $C_7H_{10}O_6$: neut. equiv., 63.3. Found: neut. equiv., 63.6.

Analytical evidence indicated that Fraction 4 was dimethyl β -phenyladipate.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.20; H, 7.20; sapon. equiv., 125. Found: C, 66.29; H, 7.18; sapon. equiv., 123.

Acid hydrolysis of a small amount of this material produced a solid acid. After recrystallization from water, it was obtained in the form of white plates, m. p. 147–148° (Manske¹³ gave the melting point of β phenyladipic acid as 146° and Price and Karabinos¹⁴ have reported the melting point to be 147–148°). A mixed melting point determination with a known sample of β -phenyladipic acid showed no depression.

Anal. Calcd. for $C_{12}H_{14}O_4$: neut. equiv., 110.5. Found: neut. equiv., 111.

The residue from the above-mentioned distillation was subjected to distillation under the low pressure obtained with a mercury-vapor diffusion pump. The separation of these high-boiling esters was not good; in no case was an analytically pure sample obtained. Table V shows the fractions obtained:

TABLE V

Compound	Weight (g.)	n_D^{20}
1 Tetramethyl hexane-1, α , γ ,6-tetracarboxylate	3.53	1.4643
2 Trimethyl α -phenylhexane-1, γ ,6-tricarboxylate	2.66	1.4963
3 Uncharacterized	2.72	
4 Residue	1.50	

The center portion of Fraction 1 gave the following analytical values:

Anal. Calcd. for $C_{14}H_{22}O_8$: C, 52.83; H, 6.91; sapon. equiv., 79.5. Found: C, 54.90; H, 6.52; sapon. equiv., 82.0.

Acid hydrolysis of this substance produced a viscous, brown, water-soluble liquid. After standing for several days, the liquid deposited a small amount of a tan colored powder. Recrystallization from acetone yielded white prisms; m. p. 116–132° with decomposition. This substance was extremely soluble in water; alcohol and acetone and insoluble in ether, benzene and petroleum ether.

Anal. Calcd. for $C_{16}H_{14}O_8$: C, 45.80; H, 5.34; neut. equiv., 65.5. Found: C, 46.83; H, 5.93; neut. equiv., 74.5.

Hexane-1,3,4,6-tetracarboxylic acid has been reported by Silberrad¹⁵ and Sell and Easterfield¹⁶ to melt at 215° with decomposition. Its dimethyl ester, prepared by Sell and Jackson¹⁷, melted at 133°. Ingold and Shoppe¹⁸ have stated the melting point of hexane-1,2,4,6-tetracarboxylic acid to be 206–207°.

A center portion of Fraction 2 gave the data:

Anal. Calcd. for $C_{18}H_{24}O_6$: C, 64.29; H, 7.14; sapon. equiv., 112. Found: C, 61.73; H, 6.53; sapon. equiv., 106.

No solid compound could be isolated from the acid hydrolysis of this fraction.

The uncharacterized distillate was redistilled and collected in small portions of 0.25–0.30 gram. Values of the refractive indices of these portions were relatively high and varied from 1.4905 for the first portion to 1.5094 for the last. Carbon and hydrogen analyses paralleled these changes and varied from 59.67 and 6.97 per cent to 61.00 and 7.02 per cent, respectively. A center portion had a molecular weight of 375 and a saponification equivalent of 95; calculated for pentamethyl octanepentacarboxylate: C, 53.47; H, 6.93; molecular weight, 404; sapon. equiv., 80.8; calculated for tetramethyl phenyl-octanetetracarboxylate: C, 62.56; H, 7.11; molecular weight, 422; sapon. equiv., 105.5.

The water-insoluble acids (6.3 grams), which were completely soluble in aqueous sodium carbonate, were esterified with a large excess of dry methanol containing 7 to 8 per cent of hydrogen chloride in a manner identical with that employed for the water-soluble acids. The resulting esters (5.05 grams) were distilled from a bulb with a low side-arm using a mercury-vapor pump. The distillate weighed 3.10 grams. It was redistilled and the product was collected in small portions of 0.35–0.50 gram. Plotting the refractive indices of these small fractions against the cumulative weight of the product gave a smooth curve with no breaks. The refractive index (n_D^{20}) varied from 1.4960 to 1.5320. All portions were viscous, yellow colored liquids, and the viscosity increased from fraction to fraction. The following analytical data were obtained from a center portion: C, 68.79; H, 7.40; molecular weight, 343; sapon. equiv., 160. Analytical data for dimethyl diphenyl-suberate, $C_{22}H_{26}O_4$, are: C, 74.58; H, 7.34; molecular weight, 354; sapon. equiv., 177.

B. Sample G-23.—The rubber sample G-23 used in this study was made by the United States Rubber Company at Naugatuck, Connecticut. It was pre-

pared by the standard process, except that only 0.15 per cent of modifier was employed. Tests in this Laboratory have shown that this sample is less than 30 per cent soluble in benzene.

Apparently because of the low solubility in chloroform, samples of G-23 required about 5 per cent longer for ozonization than like samples of G-1. At the end of the ozonization periods, the polymer had dissolved completely, however. The other procedures were the same as those employed for G-1. Very similar curves (refractive index *vs.* cumulative yield) and identical degradation products were obtained at all stages. For these reasons the experimental results for G-23 are presented in table form only.

TABLE VI

Rubber (g.)	80.0
After extraction (g.)	74.4
Volatile acids (calcd. as formic acid) (g.)	12.5
Water-soluble acids (g.)	103.6
Succinic acid from water-soluble acids (g.)	22.8
Esters from remainder of water-soluble acids (g.)	76.1
Water-insoluble acids (g.)	12.5
Esters from water-insoluble acids (g.)	11.27

TABLE VII

ESTERS FROM WATER-SOLUBLE ACIDS

Ester	Weight (g.)
1 Dimethyl succinate	28.16
2 Dimethyl fumarate (?)	2.1
3 Trimethylbutane-1,2,4-tricarboxylate	18.84
4 Dimethyl β -phenyladipate	6.55
5 Tetramethylhexane 1,x,y,6-tetracarboxylate	5.15
6 Trimethyl α -phenylhexane-1,y,6-tricarboxylate	3.85
7 Uncharacterized	4.59
8 Residue	3.5

TABLE VIII

ESTERS FROM WATER-INSOLUBLE ACIDS

Ester	Weight (g.)
1 Distillate	7.63
2 Residue	2.1

II. MEASUREMENT OF TERMINAL VINYL GROUPS

The rubber sample was torn into small pieces and extracted with the ethanol-toluene azeotrope. After drying under reduced pressure, the sample was dissolved in purified chloroform and a small amount of the solution was evaporated to determine the rubber concentration. An aliquot part was withdrawn and treated with ozonized oxygen for two and one-half hours at a rate of approximately 125 cc. per minute. The concentration of ozone was about 4 per cent.

At the end of the ozonization period, the solvent was removed by means of an aspirator at a temperature of about 40°. Distilled water was added to the dry ozonide and the mixture was subjected to steam distillation. The distillate was then analyzed for formic acid and formaldehyde by the method of Reid and Weihe⁸. The amount of carbon dioxide obtained was used for the calculation of the ozonization numbers given in Table III.

ACKNOWLEDGMENT

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SUMMARY

1. Two samples of the GR-S copolymer of butadiene and styrene were degraded by means of ozonolysis. A number of fragments were isolated and identified so that an approximate idea of the structures of the copolymers was obtained.

2. A series of butadiene copolymers was treated with ozone in an attempt to determine the extent to which the butadiene had polymerized by 1,2-addition in contrast to 1,4-addition. Although the analytical procedure employed afforded only relative values, referred to as ozonization numbers, the results indicate that the manner in which the butadiene molecule enters the growing copolymer chain is not greatly influenced by experimental conditions.

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THE STRUCTURE OF A MIXED POLYMER OF BUTADIENE AND ACRYLONITRILE *

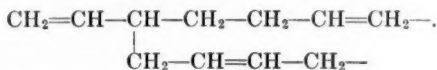
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In general, two-component polymers can be divided into two classes: (1) polymers in which each one of the components has polymerized independently and entered alone into a macromolecular structural unit, and (2) polymers in which both components take part in the structure of the same unit and, therefore, alternate in some way in the macromolecule. The question in which class a polymer belongs can be solved by chemical means only by decomposition. For high molecular-weight compounds, the most effective method appears to involve the use of the Harries method of ozonolysis. Harries used this method in investigating the structure of natural rubber. Later the method was employed both for this purpose and for explaining the structures of different types of synthetic rubber by Pummerer¹ and Klebanskiĭ and Vasil'eva².

For the clarification of the structure of mixed polymers of butadiene and acrylonitrile the method of ozonolysis was used in the work described in the present paper. If each component polymerizes separately, the products of ozonolysis on further oxidation would be expected to yield succinic acid in the case of polybutadiene, whereas polyacrylonitrile probably does not react with ozone but merely forms high-molecular weight polycarboxylic acids by saponification.

The experimental results show that treatment of the polymer with ozone, followed by oxidation of the ozonides with hydrogen peroxide, yields a decomposition product that contains an amount of succinic acid corresponding to 17 per cent of the butadiene present, and amounts of butanetricarboxylic acid, hexanetetracarboxylic acid, and dodecanepentacarboxylic acid that correspond to 81.6 per cent of the acrylonitrile present and 60.4 per cent of the butadiene present. The formation of these latter acids can result only from the presence of a pair of different structural units in the same macromolecule. The formation of butanetricarboxylic acid itself might be the result of ozonizing a polymer from 100 per cent butadiene of the structure:

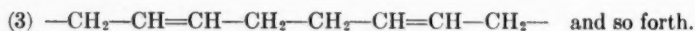
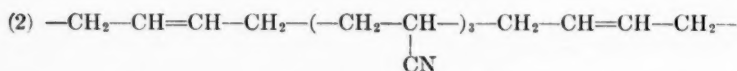
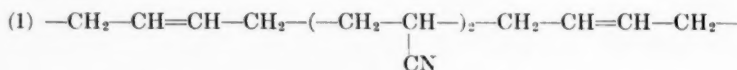


However, the formation of butanetricarboxylic acid in this manner ought to be accompanied by the formation of equivalent amounts of formic acid; actually the formic acid formed is of the order of 0.1 gram and is always accompanied by the formation of hydrochloric acid. This observation leads to the conclusion that the observed formic acid is formed from chloroform. In view of the quantitative relationship between the various products of ozonolysis,

* Translated by H. K. Livingston for RUBBER CHEMISTRY AND TECHNOLOGY from the *Journal of General Chemistry* (U.S.S.R.), Vol. 15, No. 9, pages 1426-1430 (1939).

it must be concluded that the macromolecules of the mixed polymer undoubtedly are constructed to a considerable degree from alternating molecules of butadiene and acrylonitrile.

To a lesser degree, the macromolecules are made up of several structural units, such as:



For ozonized mixed polymers with a deficiency of acrylonitrile, there is less succinic acid and more butanetricarboxylic acid.

EXPERIMENTAL PART

Equivalent amounts of butadiene and acrylonitrile were polymerized in the presence of 1 per cent of benzoyl peroxide at 60° C for 116 hours. The starting materials were removed and also low-molecular weight volatile polymers were distilled off in a high vacuum at room temperature. The polymers were transparent and yellow. For determining the percentage of acrylonitrile in the polymers, Kjeldahl analyses were made. The polymers were cut into fine pieces, immersed in dry chloroform, and allowed to stand for one day. The polymers were insoluble in chloroform, but they were greatly swollen. Ozonolysis was carried out with a small amount (2.0–2.5 grams) of polymer at 0° C. A mixture of oxygen and ozone containing 6.5–7.5 per cent of ozone was added; the rate of addition was 400–500 cc. per minute. The change in the outward appearance of the solution was used as an index of the progress of ozonolysis. The original transparent swollen polymer changed to a very viscous, almost solid, white mass, which settled out on the walls of the container. Ozonolysis was discontinued when the solution acquired a blue color, due to excess ozone. The chloroform was distilled off under reduced pressure. The ozonides were decomposed by heating on a water bath with 3 per cent of hydrogen peroxide till dissolved. Excess hydrogen peroxide was decomposed with a small amount of platinum black. Water was driven off under reduced pressure at 40°C. Then 10 cc. of additional hydrogen peroxide was added, and the mixture again distilled to dryness to accomplish complete removal of the minor portions of hydrogen chloride and formic acids that are formed as a result of the decomposition of chloroform by ozone. To separate the mixed acids by conversion to the methyl esters, the resulting syrup was dissolved in absolute methyl alcohol containing 10 per cent of dry hydrogen chloride. The mixture was allowed to stand for 24 hours at room temperature, and then was heated on a water bath for one hour. Two-thirds of the alcohol was distilled off under reduced pressure, and the ammonium chloride that crystallized was filtered off. The solution was diluted with five parts by volume of water, whereupon an oil separated out with difficulty. The oil was removed by ether extraction, the ether extract was washed with a 3 per cent solution of soda and then with water, and finally the extract was dried with calcium chloride. The resulting esters were distilled at 3 mm. pressure. The main fraction was redistilled before analysis.

ANALYTICAL DATA

Analyses were made on an initial 19.82 grams of polymer.

Kjeldahl analysis:

0.4200 g. substance, 9.67 cc. 0.5 *N* H₂SO₄, 1.78 cc. 0.5 *N* KOH.

This indicates the original polymer contained 47.32 per cent acrylonitrile.

Analyses were made on the 3.2 grams of unchanged polymer that remained after ozonolysis.

Kjeldahl analysis:

0.2209 g. substance, 9.65 cc. 0.5 *N* H₂SO₄, 8.06 cc. 0.5 *N* KOH.

The residue therefore contained 18.32 per cent of acrylonitrile. Therefore, the 16.62 grams of polymer that took part in the reaction with ozone contained 8.8 grams of acrylonitrile and 7.8 grams of butadiene.

A 0.82-gram portion of the acid obtained by the ozonolysis of 15.8 grams of polymer (corresponding to 8.40 grams of acrylonitrile and 7.47 grams of butadiene) was utilized for analysis. From this quantity the theoretical amount of acid was 30.55 grams of acid; 31.1 grams was obtained. Determination of the acrylonitrile content in this acid fraction:

(1) Distillation of ammonia under alkaline conditions:

0.2414 g. substance, 9.65 cc. 0.5 *N* H₂SO₄, 7.15 cc. 0.5 *N* KOH.

Found, 8.55 g. acrylonitrile.

(2) Kjeldahl analysis:

0.2425 g. substance, 9.65 cc. 0.5 *N* H₂SO₄, 7.18 cc. 0.5 *N* KOH.

Found, 8.39 g. acrylonitrile.

Esterification was carried out with 30 grams of acid (corresponding to 8.1 grams of acrylonitrile and 7.2 grams of butadiene). Ether extraction yielded 22 grams of complex esters. The esters were distilled in a vacuum at 3 mm. abs. For distillation, five fractions were taken as follows:

I. Fraction of 2.5 gram, boiling at 58° C:

Molecular-weight determination (cryoscopic):

0.1830 g. substance, 8.3503 g. AcOH, $\Delta t = 0.575^\circ$

0.3729 g. substance, 8.3503 g. AcOH, $\Delta t = 1.155^\circ$

Found, molecular weight = 148.8; 150.8.

Saponification number determination:

0.2510 g. substance, 50 cc. 0.5 *N* KOH, 43.08 cc. 0.5 *N* H₂SO₄

Found, equivalent weight = 72.5

Found, molecular weight = $72.5 \times 2 = 145$.

Calculated for C₆H₁₀O₄; molecular weight = 146.

Ultimate analysis:

0.1929 g. substance, 0.3491 g. CO₂, 0.1290 g. H₂O

Found, 49.34% C, 6.96% H.

Calculated for C₆H₁₀O₄, 49.31% C, 6.84% H.

The analysis of this fraction corresponds to that expected for the dimethyl ester of succinic acid.

II. Fraction of 1 gram, boiling 59–112° C:

Molecular-weight determination:

0.2187 g. sample, 9.75 g. acetic acid, $\Delta t = 0.500$

Found, molecular weight = 175.

Molecular weight of C₆H₁₀O₅ is 162.

Saponification equivalence determination:

0.1109 g. substance, 50 cc. 0.5 *N* KOH, 47.51 cc. 0.5 *N* H₂SO₄

Found, equivalent weight = 89
molecular weight = $89 \times 2 = 178$.

Ultimate analysis:

0.1352 g. substance, 0.2200 g. CO_2 , 0.0774 g. H_2O

Found, 45.01% C, 6.30% H.

Calculated for $\text{C}_6\text{H}_{10}\text{O}_5$, 44.44% C, 6.17% H.

The analysis of this fraction corresponds to that expected for the dimethyl ester of hydroxysuccinic acid.

III. Fraction of 13 grams, boiling at 130°C :

Molecular-weight determination:

0.2805 g. substance, 9.741 g. acetic acid, $\Delta t = 0.501^\circ$

Found, molecular weight = 224.6

Molecular weight of $\text{C}_{10}\text{H}_{16}\text{O}_6$ is 232.

Saponification equivalence determination:

0.2139 g. substance, 40 cc. 0.5 N KOH, 37.60 cc. 0.5 N H_2SO_4

Found, equivalent weight = 78.5

molecular weight = $78.5 \times 3 = 235.5$.

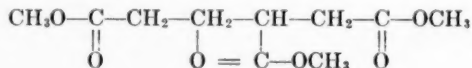
Ultimate analysis:

0.1896 g. substance, 0.3586 g. CO_2 , 0.1195 g. H_2O

Found, 51.65% C, 7.07% H

Calculated for $\text{C}_{10}\text{H}_{16}\text{O}_6$, 51.72% C, 6.94% H.

The analysis of this fraction corresponds to that expected for the trimethyl ester of butanetricarboxylic acid:



IV. Fraction of 2.4 grams, boiling at $190\text{--}202^\circ\text{C}$:

Saponification equivalence determination:

0.1819 g. substance, 50 cc. 0.5 N KOH, 45.45 cc. 0.5 N H_2SO_4

Found, equivalent weight = 80

Calculated for $\text{C}_{14}\text{H}_{22}\text{O}_8$, equivalent weight = 79.5

Found, molecular weight = $80 \times 4 = 320$.

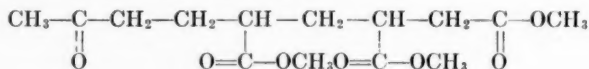
Ultimate analysis:

0.1926 g. substance, 0.3707 g. CO_2 , 0.1183 g. H_2O

Found, 52.63% C, 6.88% H

Calculated for $\text{C}_{14}\text{H}_{22}\text{O}_8$, 52.83% C, 6.91% H.

The analysis of this fraction corresponds to that expected for the tetramethyl ester of 1,2,4,6-hexanetetracarboxylic acid:



V. Fraction of 0.6 gram, boiling $210\text{--}30^\circ\text{C}$:

Saponification equivalence determination:

0.3120 g. substance, 50 cc. 0.5 N KOH, 42.80 cc. 0.5 N H_2SO_4

Found, equivalent weight = 86.

In view of the fact that polycarboxylic acids often form incomplete esters on esterification, which are appreciably soluble in water and form soluble salts with alkali metals, an investigation was also made of the aqueous layers obtained by washing the ether extract with soda solution and water.

AQUEOUS SOLUTION

Water was removed under reduced pressure, and the residue was carefully dried in a vacuum and extracted with absolute methanol. Dissolved salts were precipitated with absolute ether. This operation was repeated several times, but the syrup was not completely freed of ammonium chloride even so. The syrup was dried in a vacuum. The total weight of syrup was 4.5 grams. Analysis of syrup:

Determination of the NH_4Cl

(a) Determination of the chloride ion by titrating with 0.1 *N* AgNO_3 :
0.1785 g. substance required 33.35 cc. 0.1 *N* AgNO_3 .

(b) Determination of NH_3 by distillation from alkaline solution:
0.5245 g. substance, 20 cc. 0.5 *N* H_2SO_4 , 17.17 cc. 0.5 *N* KOH
 NH_4Cl content = 0.65 g.

Determination of the equivalent weight by titrating with 0.1 *N* NaOH :
0.3183 g. substance requires 9.20 cc. 0.1 *N* NaOH
Found, equivalent weight = 301

Calculated for $\text{C}_{13}\text{H}_{20}\text{O}_8$, 292.

The analysis corresponds to that expected for a trimethyl ester of hexane-tetracarboxylic acid.

2. ALKALINE SOLUTION

The solution was acidified with hydrochloric acid and treated by the same process used with the aqueous solution. After four treatments with ether, there remained 2.9 grams of syrup, containing 0.0015 gram of ammonium chloride.

Determination of the equivalent weight by titrating with 0.1 *N* NaOH :
0.4140 g. substance required 9.08 cc. 0.1 *N* NaOH

Found, equivalent weight = 455

Determination of the saponification equivalence with KOH :

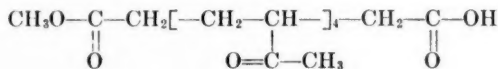
0.3251 g. substance, 50 cc. 0.5 *N* KOH , 41.52 cc. 0.5 *N* H_2SO_4

Found, equivalent weight = 76.6

molecular weight = $76.6 \times 6 = 459.6$

Calculated for $\text{C}_{21}\text{H}_{32}\text{O}_{12}$, 476.

The analysis corresponds to that expected for the pentamethyl ester of dodecanehexacarboxylic acid:



0.2500 g. substance, 0.3593 g. CO_2 , 0.0163 g. H_2O

Found, 52.70% C, 6.55% H

Calculated for $\text{C}_{21}\text{H}_{32}\text{O}_{12}$, 52.93% C, 6.72% H.

Thus 30 grams of acid, resulting from 15.3 grams of polymer containing 8.1 grams of acrylonitrile and 7.2 grams of butadiene, was separated as follows:

2.5	g. $\text{C}_6\text{H}_{10}\text{O}_4$	corresponding to 0.89 g. butadiene
1	g. $\text{C}_6\text{H}_{10}\text{O}_5$	corresponding to 0.32 g. butadiene
13	g. $\text{C}_{10}\text{H}_{16}\text{O}_6$	corresponding to 2.9 g. butadiene
3	g. $\text{C}_{14}\text{H}_{22}\text{O}_8$	corresponding to 0.5 g. butadiene
3.85	g. $\text{C}_{13}\text{H}_{20}\text{O}_8$	corresponding to 0.63 g. butadiene
2.9	g. $\text{C}_{21}\text{H}_{42}\text{O}_{12}$	corresponding to 0.32 g. butadiene.

The sum of these corresponds to 5.43 grams of butadiene, which is 77 per cent of the initial value.

- 13 g. $C_{10}H_{16}O_6$ corresponding to 2.9 g. acrylonitrile
- 3 g. $C_{14}H_{22}O_8$ corresponding to 1.06 g. acrylonitrile
- 3.85 g. $C_{13}H_{20}O_8$ corresponding to 1.36 g. acrylonitrile
- 2.9 g. $C_{21}H_{32}O_{12}$ corresponding to 1.29 g. acrylonitrile.

The sum of these products corresponds to 6.61 grams of acrylonitrile, which is 81.6 per cent of the initial value.

SUMMARY

1. In copolymers of butadiene and acrylonitrile, both components enter into the constitution of the macromolecules.
2. Approximately one-half the polymer is composed of macromolecules, in which the two monomer structures exactly alternate in the macromolecular skeleton.
3. Approximately one third of the polymer is constructed from macromolecular units in which each molecule of butadiene is placed between two or three molecules of acrylonitrile.

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KINETICS AND OPTIMUM PHENOMENON OF VULCANIZATION *

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The fundamental process of vulcanization consists in the combination of rubber with a vulcanizing agent: sulfur, sulfur monochloride, *etc.* The kinetics of this process may be expressed by monotonous curves. These may be interpreted either as the result of the heterogeneous character of the reaction¹ or as the result of the combination of several homogeneous reactions². At the same time that the rubber combines with the vulcanizing agent, and largely as a consequence of this, a number of its physical-chemical and mechanical properties—solubility, density, tensile strength and other properties—undergo a change. These changes are extremely interesting from the technological point of view. In distinction to the kinetics of the combination of rubber with the vulcanizing agent, the kinetics of these processes can in most cases be represented by curves with a maximum or minimum. Thus, in the vulcanization of crude rubber, the tensile strength and modulus change according to a curve having a maximum; the solubility change follows a curve with a minimum. This character of the change experienced by the principal technical properties of the rubber determines the so-called "vulcanization optimum". This term refers to that moment in the process of vulcanization when the particular property attains the necessary maximum or minimum, depending on the technical purposes of the vulcanizate.

Proceeding on the supposition that the changes in properties of the rubber during vulcanization take place by the simultaneous action of multidirectional factors, one of the authors of the present paper³ was the first to advance a qualitative explanation of the specific character of the kinetics curves and optimum phenomenon of vulcanization. In technical vulcanization there are at least two processes to be considered:

- (1) interaction of the rubber with the vulcanizing agent;
- (2) interaction of the rubber with molecular oxygen, which is always present in any rubber mixture.

The vulcanizing agent has a structural function, *i.e.*, it enters the molecular chains, thus increasing their molecular weight and uniting them into more complicated forms. On the other hand, the molecular oxygen in crude rubber mixtures at a certain stage of the interaction causes disintegration of the molecular chains of the rubber; *i.e.*, is responsible for the process of so-called oxidizing destruction⁴. The combination of these processes, operative in opposite directions, yields an overall (experimental) kinetics curve which can have a maximum or a minimum, according to the kinetics of the elementary processes and their influence on the particular property of the vulcanizate.

* Reprinted from the *Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS*, Vol. 53, No. 4, pages 327-330, 1946.

From this point of view it appears feasible to examine the kinetics of the change experienced by such an important property as durability during the vulcanization of crude rubber by sulfur. (Figure 1.)

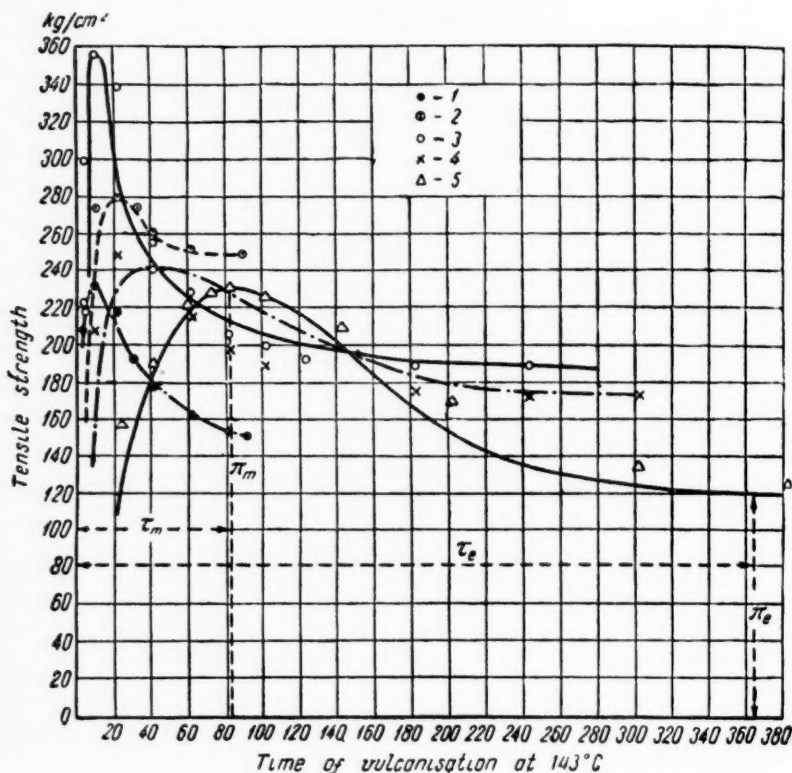


FIG. 1.

As a result of the interaction with the vulcanizing agent, the durability of the vulcanizate increases. This is due both to the increase in the forces of cohesion between the molecules, owing to the introduction of sulfur atoms into the rubber chain, and to the establishment of bonds between the chains through these atoms (a process of "sewing together" of the molecules). It can be asserted in the first approximation that the durability of the vulcanizate increases in proportion to the amount of combined sulfur, the proportion factor depending on the composition of the mixture and conditions of vulcanization. This assertion is based, on the one hand, on the consideration that the molecular forces of attraction are additive, and that, consequently, the increase in durability, which takes place at the expense of the substitution of polar atoms of sulfur for the double bonds, is proportional to their content in the vulcanizate. On the other hand, our experiments have shown that the amount of bridging, i.e., connecting the different molecular chains of rubber to one another by sulfur, determined by the method of interaction with methyl iodide⁵, is a linear function of the total proportion of combined sulfur in the vulcanizate (Figure 2).

As for the simultaneous action of the oxygen, numerous observations⁶ show that the durability of the vulcanizate diminishes in proportion to the proportion of combined oxygen.

Hence, we may write:

$$\pi = (b_1 + a_1 S)(b_2 - a_2 O) \quad (1)$$

where π is the tensile strength of the vulcanizate at a given moment of vulcanization; S is the amount of sulfur combined with the rubber; O , the amount of combined oxygen; and b_1 , b_2 , a_1 and a_2 are constants.

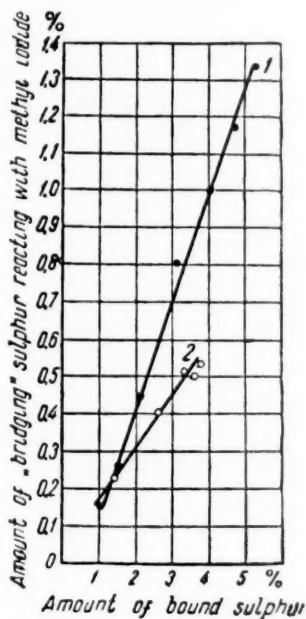


FIG. 2.

	1	2
Light crepe	100	100
Sulfur	8	5
Diphenylguanidine	—	1
Zinc oxide	—	3

According to data of Lewis², the kinetics of the combination with sulfur in the preparation of soft rubbers can be described by the following equation:

$$S = S_0(1 - e^{-k_1 \tau}) \quad (2)$$

where S_0 is the initial content of the sulfur in the mixture; S , the amount of combined sulfur at the moment τ ; and k_1 is the constant of the rate of the combination with sulfur.

The combination of rubber with oxygen is usually expressed by the equation of autocatalytic reaction⁷:

$$dO/d\tau = k(O_0 - O)(A + O) \quad (3)$$

which, for cases where the initial molar concentration of the catalyst exceeds the concentration of the reagent, gives the expression:

$$O \approx O_0(1 - e^{-k(O_0+A)\tau}) \approx O_0(1 - e^{-k_2\tau}) \quad (4)$$

where O is the amount of oxygen combined at the moment τ ; O_0 , the maximum amount of oxygen in the mixture which can possibly combine with the rubber; A , a constant corresponding to the initial content of the catalyst; k the kinetic constant. This is precisely the case with the vulcanization of rubber, since the mixture contains peroxide compounds and accelerators of vulcanization, which in most cases are oxidation catalysts.

Substituting (2) and (4) in (1), and introducing the symbols:

$$b_1b_2 = \pi_0; \quad \frac{a_1S_0}{b_1} = a; \quad \frac{a_2O_0}{b_2} = b$$

where π_0 , as can be seen from (1), determines the durability of the crude mixture, we obtain:

$$\pi = \pi_0[1 + a(1 - e^{-k_1\tau})][1 - b(1 - e^{-k_2\tau})] \quad (5)$$

The constant k_1 can be determined from the kinetics curve of combination with sulfur; the constant k_2 , from the kinetics curve for combination with oxygen. Consequently, Equation (5) contains only two constants a and b , which can be determined from the kinetics curve of the change in durability.

To determine these coefficients let us rewrite Equation (5) in the form:

$$\pi/\pi_0 = (1 + ax)(1 - by)$$

where $x = 1 - e^{-k_1\tau}$ and $y = 1 - e^{-k_2\tau}$. Let us denote by π_m the maximum durability, corresponding to the optimum of vulcanization (Figure 1), and by π_l the durability in the state of equilibrium, for which the following condition is apparently observed:

$$e^{-k_1\tau} \approx e^{-k_2\tau} \approx 0$$

and consequently, $x \approx y \approx 1$. Then:

$$\pi_m/\pi_0 = (1 + ax_m)(1 - by_m), \quad \pi_l/\pi_0 = (1 + a)(1 - b)$$

Making the substitution:

$$u = \frac{1 - y_m}{y_m}(1 + a), \quad v = \frac{1 - x_m}{x_m}(1 - b)$$

we obtain the system of equations:

$$\left. \begin{aligned} u + v &= \frac{\pi_m}{\pi_0 x_m y_m} - \frac{\pi_l}{\pi_0} - \frac{(1 - x_m)(1 - y_m)}{x_m y_m} \\ uv &= \frac{\pi_l(1 - x_m)(1 - y_m)}{\pi_0 x_m y_m} \end{aligned} \right\} \quad (6)$$

Solving system (6) and taking into consideration that $uv \ll u + v$, and the derivative $d\pi/d\tau$ is positive when $\tau = 0$, we arrive at the following expressions for the coefficients a and b of Equation (5):

$$a = \left(\frac{\pi_m}{\pi_0 x_m y_m} - \frac{\pi_l}{\pi_0} \right) \frac{1 - y_m}{y_m} - 1, \quad b = 1 - \frac{\pi_l}{\pi_0(1 + a)}$$

The applicability of the derived Equation (5) has been confirmed by numerous examples of the vulcanization of mixtures of various compositions, both in our experiments and in the experiments of other authors⁸. Figure 1 gives kinetic curves for some of these mixtures, the separate points representing the values of durability calculated according to Equation (5). The mixtures contain different accelerators (1 contains dimethyldithiocarbamate; 2, heptaldehydeaniline; 3, tetramethylthiuram disulfide; 4, mercaptobenzothiazole; 5, diphenylguanidine). The graph shows that the equation proposed represents quite satisfactorily the kinetics of the vulcanization process. This undoubtedly lends support to the concept defended by the authors of the present paper, viz., the concept of vulcanization as a combination of several multidirectional processes of which some are structuralizing, whereas others act in the opposite direction.

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THE CHEMISTRY OF RUBBER THE INTERACTION OF ETHYLENIC COMPOUNDS AND RUBBER *

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INTRODUCTION

It is known that the hydrocarbon of rubber has an ethylenic structure; its chemical reactions, the basic principles of which were brought out in 1902 by Weber¹, and which were the object, in 1930, of important work by Fisher², show that it has the general properties of ethylene derivatives, including the addition of hydrogen and metalloids of the first group (chlorine and bromine in particular), the addition of hydracids, scission by ozone, autoxidation, and isomerization by means of catalysts which isomerize ethylene derivatives, such as sulfuric acid and chlorides of metalloids.

However, aside from these general reactions, rubber hydrocarbon reacts in other ways which likewise depend on the unsaturation of the molecule and on the macromolecular structure, and which in this particular case are of prime importance because it is on these properties that the processing and applications of rubber depend.

As a good example, a fundamental change results from the action of sulfur, *viz.*, vulcanization, whereby rubber passes from a predominantly plastic state to a predominantly elastic state, a change which is manifest by the rubber becoming insoluble. Moreover, sulfur is not the only agent which is capable of bringing about vulcanization; in fact, it has been found that many other agents are capable of vulcanizing rubber. Although Goodyear discovered this reaction in 1839, there is still no general agreement as to the mechanism of vulcanization; however, vulcanization is at present regarded as the transformation of an agglomerate of filiform molecules into a three-dimensional network.

In any event, it should be pointed out that the term *vulcanization* is a technical term which should be reserved for the formation of elastic products which have certain definite properties; it does not, therefore, necessarily include all the changes which involve an increase in molecular size as the result of the formation of what might be called anastomoses, uniting originally isolated filiform molecules³.

In contrast to this type of transformation, rubber is capable of undergoing the reverse phenomenon, *i.e.*, molecular degradation, whereby the products which are obtained are composed of smaller molecules. This process amounts practically to autoxidation, in which numerous compounds have no effect other than that of catalysts.

Incidentally it should be added that certain reagents are capable of playing a part in the reaction in one way or another, depending on the conditions under

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Bulletin de la Société Chimique de France*, 5th Series, Vol. II, No. 10-11, pages 553-561, November-December 1944.

which they are used. A good example is the action of oxygen on rubber solutions. In general, oxygen brings about degradation, which is manifest in a lowering in viscosity of the solutions; on the contrary, oxygen can, under certain conditions, bring about gelation.⁴

Finally may be mentioned a fact which adds to the chemistry of rubber, *viz.*, that not only can seemingly unimportant factors bring about opposite transformations, but that, except under a few conditions, the reactions of rubber hydrocarbon are far from simple. Several phenomena may take place simultaneously and finally bring about changes which chemically are ill defined⁵. However, in spite of this, it has been possible to reproduce these phenomena in an empirical way, and thus to obtain useful transformation products, *e.g.*, chlorinated rubbers, hydrochlorinated rubbers, cyclized rubbers, isomerized rubbers, and oxidized rubbers, which have extended the applications of rubber to paint and varnishes (chlorinated rubber, Rubbone, Pliolite), to molding powders (Plioform), and to transparent sheets (Pliofilm), and even to synthetic fibers (Tensolite).

RUBBER AND ETHYLENIC COMPOUNDS

The foregoing rapid survey of the chemistry of rubber covers the principal facts known up to 1938. At that time Bacon and Farmer⁶ described the addition of maleic anhydride to this hydrocarbon, which was carried out in solution under the influence of benzoyl peroxide. This reaction represents the beginning of an important new chapter in the chemistry of rubber, which might have been foreseen because of the ethylenic character of rubber, whereby it would react with olefinic compounds having active double bonds, notably those which are often designated by the term vinyl compounds.

It was, in fact, found by Compagnon and Le Bras⁷ in 1941 that other active ethylenic compounds, particularly acrylonitrile, are capable under certain conditions of combining with rubber hydrocarbon when they are polymerized in latex. It was at the same time discovered that this combination can be brought about equally well by an entirely different process, *i.e.*, by simply mixing these compounds into rubber, a process which is particularly easy with maleic anhydride.

It is very important to point out that, contrary to what has been assumed for a long time, this mixing operation does not consist of mechanical treatment alone. The transformations which are observed show that a chemical reaction takes place, involving oxidation by atmospheric oxygen.

This oxidation takes place with abnormal intensity, and when it involves rubber alone, is manifest chiefly by a softening or plasticization of the entire mass, as a result of a decrease in the length of the molecules.

On the other hand, when, not rubber alone, but a mixture of rubber and maleic anhydride is masticated⁸, there is observed, not the usual plasticization, but an increase in stiffness of the mass, probably as a result of the formation of larger molecules by the interaction of rubber and maleic anhydride. That such a reaction between double bonds can take place is an entirely new phenomenon, which unquestionably can be attributed to peroxides formed during mastication of the rubber⁹. As a matter of fact, peroxides, which are powerful degrading agents in the autoxidation of ethylenic compounds, are also widely used as catalysts of polymerization.

Thus the combination of rubber hydrocarbon with active ethylenic compounds appears to be a general phenomenon, which can take place under the

various conditions ordinarily used in carrying out this type of reaction, *e.g.*: (1) in solution, with maleic anhydride⁶; (2) en masse (by mastication), with maleic anhydride⁷; and (3) in emulsion (in latex), with acrylonitrile⁷.

With regard to the chemistry of this reaction, it is well to recall that even if it is known that the hydrocarbon of rubber is a polyisoprene and if, in addition, it is assumed that the macromolecules are filiform, certain peculiarities of its structure still remain in doubt. Under these conditions no attempt can be made to settle the much more complicated problem of the constitution of compounds of rubber hydrocarbon with other ethylenic compounds, and the present discussion is limited to the advancement of several hypotheses. The experiments described in the present work had as their objectives: (1) to prove that rubber actually does combine with the ethylenic compounds in question; and (2) to determine the essential properties of the different products in relation to the operating conditions.

That compounds of this type may be of practical interest has already been pointed out¹⁰, and this subject need not be discussed here.

PROOF OF THE COMBINATION OF ETHYLENIC COMPOUNDS WITH RUBBER

It is not justifiable to conclude, because the properties of rubber are changed, even to a great extent, by another substance, that there is a reaction between the two substances. As a matter of fact, a large number of reagents are known to be capable of bringing about profound changes in rubber, *e.g.*, changing it from a pliable elastic condition to hard rubber or even to a brittle yet thermoplastic state. These transformation products all have the empirical composition $(C_5H_8)_n$, and their formation has been regarded as a case of isomerization¹¹, even though in reality the value of n is not always the same. However, the term isomerization still is justified, for some change in structure certainly does take place.

In the particular case in question in the present work, the changes observed in the properties of rubber are not the result of isomerization, but rather of a union of ethylenic compounds with rubber, as can be shown by the following considerations.

*Reaction in solution*¹².—In studying the action of maleic anhydride on rubber in solution, Bacon and Farmer depended, in demonstrating that this reagent actually does add to rubber, on the increase in weight of the rubber precipitated from solution. The precipitating agent was ethanol; the rubber had then to be reprecipitated, while the uncombined maleic anhydride remained in solution. This proof would perhaps be insufficient if only small proportions of maleic anhydride had taken part in the reaction; however, since Bacon and Farmer succeeded in fixing, under certain operating conditions, more than 100 parts of maleic anhydride per 100 parts of rubber, no doubt can remain that addition actually does take place.

Furthermore the present authors have found that the reaction can be carried out in solution, not only with maleic anhydride but with acrylonitrile. Under suitable operating conditions¹³, the product obtained is soluble in benzene, and contains, according to the determination of nitrogen in the dry product, almost 10 per cent of acrylonitrile. This acrylonitrile can neither be simply mixed in an uncombined state in the rubber, because it is very volatile¹⁴, nor can it be polymerized independent of the rubber, for polymerized acrylonitrile is remarkable for its insolubility in various solvents¹⁵.

Reaction in the dry mass.—In the absence of all solvent, maleic anhydride combines with rubber by mastication of the mixture on a mill, as has been pointed out above, or even by simple heating of the two in the presence of a suitable catalyst, *e.g.*, benzoyl peroxide. These latter conditions lend themselves less well to investigation, for in this case the peroxide has itself a very marked action on the rubber¹⁶, and it is therefore difficult to distinguish between this action and that of maleic anhydride. In the present paper, the work was limited to an investigation of the reaction on a mill.

Maleic anhydride was added directly to a definite weight of rubber on a mill¹⁷, and the mixture was masticated long enough for the reaction to be complete. The increase in weight of the mass indicates the quantity of anhydride which has been added¹⁸. It is easy, by acetone extraction, to separate the maleic anhydride which has not reacted and to determine it in the extract. The amount of free maleic anhydride found in this way represents only a small fraction of the amount originally added. For example, in one experiment, after addition of 12 parts of maleic anhydride per 100 parts of rubber, the uncombined maleic anhydride (as determined in the acetone extract) was only 1.1 parts per 100 parts of rubber. The difference, 10.9 parts of maleic anhydride, represents the quantity of maleic anhydride which combined with the rubber.

Because of its insolubility, the reaction product does not lend itself readily to chemical analysis, *e.g.*, to determinations of its acid number and iodine number. However, its percentage composition, although of only relative significance because it does not represent a pure substance, indicates profound changes in chemical composition, as shown in Table I.

TABLE I
PERCENTAGE COMPOSITION OF RUBBER BEFORE AND AFTER TREATMENT
WITH MALEIC ANHYDRIDE

(In each case the analyses were made after extraction by acetone)

Constituent	Rubber combined with maleic anhydride	Original rubber
Carbon	80.4	85.9
Hydrogen	10.9	11.7

The difference, 6.3 per cent, between the total carbon plus hydrogen of the two samples may be attributed in a general way to the oxygen of the combined maleic anhydride. The value represents 12.8 per cent of the maleic anhydride, which is of the same order of magnitude as that, *viz.*, 10.9 per cent, found by the gravimetric method.

Reaction in emulsion.—In this case combination is controlled by the addition of a catalyst, *e.g.*, ethyl hydroperoxide. In these particular experiments, maleic anhydride was replaced by styrene, vinyl acetate, various acrylic esters, methacrylonitrile and acrylonitrile. Here it was much more difficult than in the preceding experiments to prove that combination of the ethylenic compounds with rubber actually takes place, for, unlike maleic anhydride, all these compounds themselves can polymerize, and it is difficult to distinguish between this polymer and the addition product with rubber, since both products are formed simultaneously in various proportions. Thus, in the reaction to which particular attention was devoted, *viz.*, that with acrylonitrile, the polymer of the latter is insoluble in all solvents. On the other hand the reaction modifies the rubber in such a way that the rubber becomes so insoluble

that it can no longer be dissolved except under special conditions, *e.g.*, in boiling *p*-dichlorobenzene, whereby its structure may be changed. This inability to separate the modified rubber from the polymerized acrylonitrile made it impossible to prove directly that there had been any chemical combination of the rubber with the acrylonitrile¹⁹.

Because of this, the reaction was followed only by indirect experimental methods, *i.e.*, by comparing the action of solvents on the products formed by coagulation of two types of emulsions.

(1) Latex in which acrylonitrile had been polymerized, and which consequently might contain both polymerized acrylonitrile and the rubber-acrylonitrile compound.

(2) A mixture of latex and a dispersion of polymerized acrylonitrile, prepared by the method of Bacon, Farmer and Schidrowitz²⁰, the coagulated product from which certainly contains rubber in unaltered form.

TABLE II

Acrylonitrile polymerized or copolymerized per 100 parts of rubber	Polymerization of acrylonitrile within the latex				Mixture of latex and polymerized acrylonitrile			
	Swelling of coagulum in solvent (percentage)		Swelling of vulcanizate in solvent (percentage)		Swelling of coagulum in solvent (percentage)		Swelling of vulcanizate in solvent (percentage)	
	Benzene	Naphtha	Benzene	Kerosene	Benzene	Naphtha	Benzene	Kerosene
0	—	—	—	—	—	—	346	190
4.3	—	—	—	—	almost wholly dissolved	—	318	184
6.2	1025	925	279	180				
20.	1000	850	221	134				
22.5	—	—	—	—	almost wholly dissolved	—	278	158
34.5	825	700	148	89				
39.	—	—	—	—	almost wholly dissolved	—	246	127
56.5	775	550	111	50				
59.6	—	—	—	—	almost wholly dissolved	—	164	89

The data shown in Table II refer in part to the action of solvents on a vulcanizate. This vulcanizate was prepared by curing for 10 minutes at 143° C, in a press, the following mixture: modified rubber or rubber + polymerized acrylonitrile, 100; sulfur, 3; piperidinium pentamethylene dithiocarbamate, 1, phenyl- β -naphthylamine, 1; stearic acid, 1; zinc oxide, 5.

The differences in properties of mixtures prepared with the same percentages of acrylonitrile²¹, as shown in Table II, prove that polymerization of acrylonitrile in a latex mixture brings about profound changes in the rubber. However, it is not justifiable to exclude *a priori* the possibility that the catalysts used to bring about the reaction (ethyl hydroperoxide, hydrogen peroxide, and ammonium persulfate) are themselves responsible for these changes in the rubber. Spence and Ferri²² have, in fact, pointed out that the part of crude rubber which is soluble in the usual solvents, and which has become generally known as sol rubber, can be decreased or increased by the action on the latex of various catalysts, in accordance with whether the operation is carried out in the absence or presence of air. However, control tests in the absence of acrylonitrile by the present authors gave coagula which in some cases were unaltered but more frequently were degraded, *i.e.*, soft, tacky, and soluble in

greater proportion in solvents. These characteristics indicate a transformation which is the reverse of that observed in the presence of acrylonitrile.

In view of these results, which show that the changes which rubber undergoes cannot be explained either by a mere mixture of rubber and acrylonitrile or by the action of catalysts alone, it is highly probable that the changes are attributable to the formation of a compound of rubber and acrylonitrile.

GENERAL CHARACTERISTICS OF THE PRODUCTS

Great difficulty is encountered when the attempt is made to compare different transformation products of rubber, for it is not possible to distinguish them by the exact physical characteristics generally used in organic chemistry.

To classify the various addition compounds obtained in the reactions of rubber with the ethylenic compounds which have just been described, recourse was had to their affinity for solvents. It is possible to obtain quantitative data by determining, on the one hand, the fraction which is dissolved in the solvent employed, and on the other hand, the extent to which the insoluble part swells in the solvent. In this way it was found, for example, that the addition products which contained approximately 10 per cent of combined ethylenic compound showed, in benzene (except as otherwise specified), the following general characteristics. These representative results show that the three procedures by which the addition reaction can be carried out do not lead to products with the same properties.

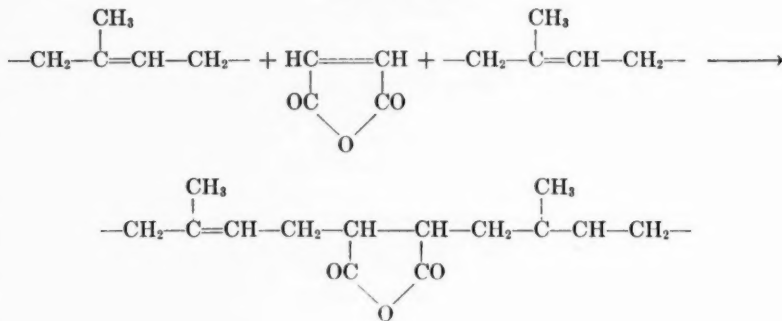
(1) *Reaction in solution*.—The products obtained under the particular experimental conditions employed (solutions of 3 per cent concentration by weight of rubber) are in general soluble in the crude state in ordinary solvents. It has already been shown¹³, moreover, that the partial insolubility found in some cases depends primarily on a specific action of the catalyst and can be avoided. In the vulcanized state, swelling is much less than that of the control samples, *e.g.*, in naphtha, it decreases to one-half its original value.

Reaction en masse in the dry state.—This procedure gives products which in the raw state are insoluble and the swelling of which is of the same order of magnitude as that of ordinary rubber-sulfur vulcanizates. In the vulcanized state the products swell less than do control samples prepared from unmodified rubber.

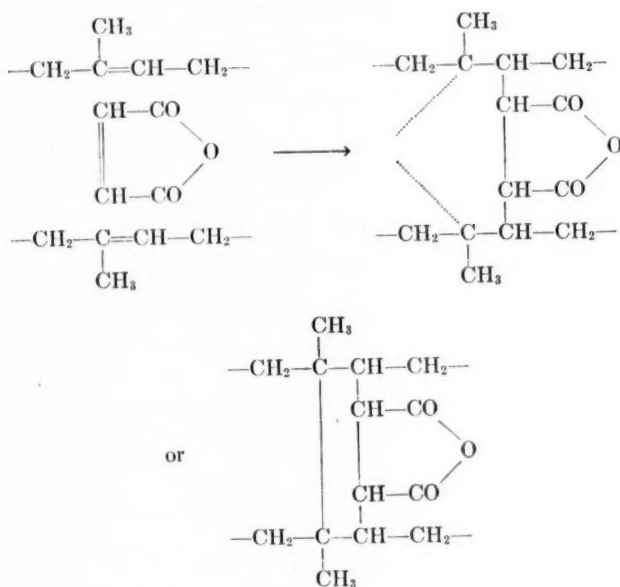
Reaction in emulsion.—In the raw state, the products are practically insoluble, but swell strongly. In the vulcanized state, swelling decreases as a function of the acrylonitrile content (see Table II). It is not, however, possible to make a strictly quantitative comparison between the products obtained by the emulsion process and those obtained by the solution process or by the dry mass process because, as has been pointed out, the percentage of acrylonitrile actually combined with the rubber is not known precisely in the products obtained by this third procedure.

In addition to these methods of differentiation, the physical appearance of the raw products also is indicative. When prepared by the solution method, the products are plastic; on the contrary, when prepared by the dry mass method, they have considerable elasticity and approach vulcanized rubber; when prepared by the emulsion process, their properties are intermediate between the other two and are difficult to define.

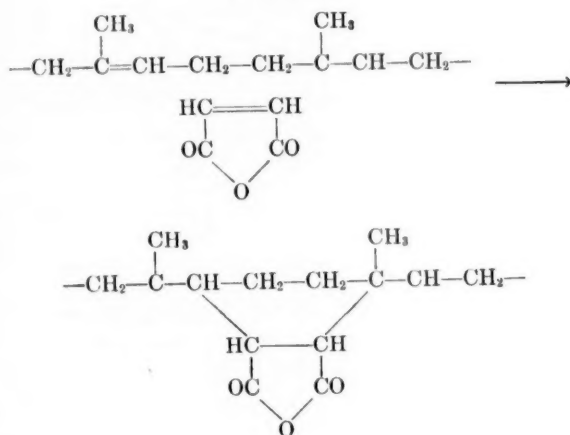
After vulcanization, all the products are less extensible and are harder than the corresponding control vulcanizates.



SCHEME II



SCHEME III



On the contrary, with other vulcanizing agents, in which case one of the elements of the second group of metalloids²⁹ always take part, either directly or indirectly, widely different reactions can be conceived, as, for example, the notable case of sulfur³⁰, the vulcanizing agent par excellence. It should be noted, however, that this latter element bears a close resemblance to vinyl monomers, both in the unsaturated state of its $S=S$ molecule and in the facility with which it can form a $-S-S-S-S-S-$ chain having elastic properties.

EXPERIMENTAL PART

Reaction in solution.—This reaction was carried out by the technique of Bacon and Farmer⁶. Rubber (7 parts), maleic anhydride (10 parts) and benzoyl peroxide (1 part) in toluene (230 parts by weight) were heated 18 hours at 100° C; the resulting modified rubber was then precipitated by adding 4 volumes of alcohol for each volume of toluene liquor; after drying in a vacuum, the product contained approximately 10 per cent of combined maleic anhydride.

The reaction was carried out under the same operating conditions with other derivatives in place of maleic anhydride, *e.g.*, itaconic anhydride, citraconic anhydride, acrylic acid, acrylonitrile, and methacrylonitrile. The yields varied greatly according to the particular ethylenic compound taking part in the reaction.

Reaction in rubber in the dry mass.—The reaction between rubber and maleic anhydride under these conditions on a mill has been described in detail by Compagnon and Bonnet¹⁷.

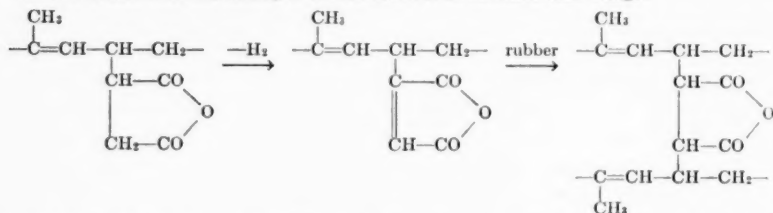
Reaction in emulsion.—An essential condition for the reaction to take place in emulsion is that ammonia be absent; consequently if ordinary latex stabilized with ammonia is used as the source of raw material, it is necessary to expel all the ammonia beforehand. A simpler way is to use a type of latex such as Revertex, which contains no ammonia in the first place.

The reaction can, for example, be carried out in the following way. Latex free of ammonia is brought to a rubber content of 20 per cent; 2 per cent (by weight) of Igepon-T (sodium oleylmethylaminoethylsulfonate), 0.5 per cent of ammonium persulfate, and 10 per cent of acrylonitrile are added in that order; and the mixture is agitated vigorously. The emulsion which is obtained is very stable. It is kept in a closed vessel for 4 days at 55° C; the gelled mass is macerated with a 5 per cent sodium bisulfite solution on a steam bath, then washed thoroughly, and dried. When the resulting product is passed through a mill, it forms a sheet resembling crepe rubber, and contains ordinarily about 35 parts of polymerized acrylonitrile per 100 parts of rubber.

REFERENCES

- ¹ Weber, "The Chemistry of India Rubber", Longmans Green, London, 1902.
- ² Fisher, *Chem. Rev.* 7, 51 (1930).
- ³ Such an effect can be observed when there is not necessarily any combination of the rubber with the reagent present.
- ⁴ Staudinger, *Proc. Rubber Tech. Conf. London*, 1938, p. 253; RUBBER CHEM. TECH. 12, 117 (1939).
- ⁵ This explains why the present authors have purposely used the term degradation and not depolymerization. Likewise the term polymerization cannot strictly be applied here to express the increase in molecular size. It would be desirable to adopt for this purpose a special term, *e.g.*, synthesis (from the Greek, union, junction), which has already been proposed by Dufraisse and Compagnon for the special case of prosthesis-synthesis reactions (*Rev. gén. caoutchouc* 18, 39 (1941); RUBBER CHEM. TECH. 19, 329 (1946)) and which could be extended to all those phenomena where molecules unite, regardless of the number or nature of the bonds involved. The corresponding adjective would be *synesic*.
- ⁶ Bacon and Farmer, *Proc. Rubber Tech. Conf. London*, 1938, p. 256; RUBBER CHEM. TECH. 12, 200 (1939).
- ⁷ Compagnon and Le Bras, *Compt. rend.* 212, 616 (1941); *Rev. gén. caoutchouc* 18, 89 (1941).

- ⁸ Le Bras, *Rev. gén. caoutchouc* **19**, 43 (1942); RUBBER CHEM. TECH. **19**, 313 (1946); Compagnon and Bonnet, *Rev. gén. caoutchouc* **19**, 79 (1942); RUBBER CHEM. TECH. **19**, 319 (1946).
- ⁹ Dufraisse and Vieillefosse, *Rev. gén. caoutchouc* **12**, 3 (1935); RUBBER CHEM. TECH. **9**, 206 (1936).
- ¹⁰ Le Bras, *Rev. gén. caoutchouc* **19**, 43 (1942); RUBBER CHEM. TECH. **19**, 313 (1946).
- ¹¹ Fisher and McCollm, *Ind. Eng. Chem.* **19**, 1328 (1927).
- ¹² The details of the operating conditions for the various reactions are given in the Experimental Part.
- ¹³ Compagnon and Delalande, *Rev. gén. caoutchouc* **20**, 133 (1943); RUBBER CHEM. TECH. **20**, 689 (1947).
- ¹⁴ A control test, in which the reaction was carried out in the absence of any catalyst, showed a practically negligible increase in nitrogen content.
- ¹⁵ Kern and Fernow, *J. prakt. Chem.* **160**, 281 (1942); RUBBER CHEM. TECH. **17**, 356 (1944).
- ¹⁶ Ostromislensky, *India Rubber World* **81**, No. 3, 55 (1929).
- ¹⁷ Compagnon and Bonnet, *Rev. gén. caoutchouc* **19**, 79 (1942); RUBBER CHEM. TECH. **19**, 319 (1946).
- ¹⁸ Strictly speaking, it would be necessary to take into account the increase in weight of the rubber when it is masticated alone, an increase resulting from fixation of oxygen from the air (cf. Cotton, *Trans. Inst. Rubber Ind.* **6**, 487 (1931); RUBBER CHEM. TECH. **5**, 153 (1932); Busse, *Ind. Eng. Chem.* **24**, 140 (1932); RUBBER CHEM. TECH. **5**, 164 (1932)); but for the times of mastication used in the work, this value is very small, i.e., less than 0.1 per cent.
- ¹⁹ It would seem possible to prove this by using, in place of acrylonitrile, methacrylonitrile, which forms a polymer which is soluble in some liquids in which rubber is insoluble.
- ²⁰ Bacon, Farmer and Schidrowitz, *Proc. Rubber Tech. Conf. London*, **1938**, p. 525; Bacon and Schidrowitz, *Trans. Inst. Rubber Ind.* **15**, 152 (1939).
- ²¹ It is not possible in such experiments to operate at will with mixtures the compositions of which are exactly the same in each case, so it was necessary to compare mixtures of closely similar compositions.
- ²² Spence and Ferri, *J. Am. Chem. Soc.* **59**, 1648 (1937); RUBBER CHEM. TECH. **11**, 47 (1938).
- ²³ Some of these probable reactions have already been suggested by one of the present authors (cf. Le Bras, *Rev. gén. caoutchouc* **19**, 43 (1942); RUBBER CHEM. TECH. **19**, 313 (1946)).
- ²⁴ See, for example, Delaby, *Bull. soc. chim.* [5] **4**, 768 (1937).
- ²⁵ Alder, Pascher and Schmitz, *Ber.* **76**, 27 (1943).
- ²⁶ Bacon and Farmer, *Proc. Rubber Tech. Conf. London*, **1938**, p. 256; RUBBER CHEM. TECH. **12**, 200 (1939). It can also be assumed, as has been done by Ch. Dufraisse in one of his recent lectures at the Collège de France, that the reaction is more complex and involves peroxides, for even when no peroxidic catalysts are added, account must always be taken of those which are formed within the mixture during mastication. After an initial substitution-addition reaction (Scheme IV), dehydrogenation by the action of peroxides should take place by the action of the peroxides, followed by a new substitution-addition reaction, leading to the formation of an intermolecular bridge:



- ²⁷ It should be recalled that the minimum amount of sulfur necessary to vulcanize rubber is only 0.15 per cent.
- ²⁸ See, for example, Le Bras and Compagnon, *Chimie & industrie* **46**, 291 (1941).
- ²⁹ Except, however, processes of vulcanization by condensation (cf. Dufraisse, and Compagnon, *Rev. gén. caoutchouc* **18**, 39 (1941); RUBBER CHEM. TECH. **19**, 329 (1946); Wildschut, *Rev. trav. chim.* **61**, 898 (1942); RUBBER CHEM. TECH. **19**, 86 (1946)).
- ³⁰ See, for example, Houwink and Van Amerongen, *Rev. gén. caoutchouc* **19**, 293 (1942).
- ³¹ Compagnon and Bonnet, *Rev. gén. caoutchouc* **19**, 79 (1942); RUBBER CHEM. TECH. **19**, 319 (1946).

TWO METHODS OF PROTECTION AGAINST OXYGEN AND THE IMPROVEMENT WHICH RESULTS FROM THEIR COMBINED USE.* I. OBSERVATIONS ON THE MECHANISM OF PROTECTION

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INTRODUCTION

It is now known that antioxygenic substances protect oxidizable materials against the deleterious action of oxygen by retarding their rate of combination with this element. On this principle rests the technique developed by Moureu and Dufraisse¹ for studying the phenomenon of antioxygenic action, by means of which it has been possible to make many interesting observations. However, the concept of autoxidation presupposes that, from the point of view of secondary effects, the results should be the same whether an antioxygenic agent hinders the formation of peroxides or modifies their activity; for example, by catalyzing their destruction or their rapid transformation into less active forms having diminished catalytic power or even no catalytic power at all².

In any event it is this diminution of oxidizability which has, up to the present time, been found to be a general phenomenon characteristic of rubber, and of other substances which can be protected by antioxygenic agents.

As a matter of fact, as far as rubber itself is concerned, experiments by different investigators are in accord with this concept. For example, Dufraisse and Drisch³ found that phenyl- β -naphthylamine, aldol- α -naphthylamine, *m*-toluylenediamine, and hydroquinone definitely reduce the rate of oxidation. Kohman⁴ has published curves which show the retarding effects obtained with various antioxygenic substances. Ingmanson and Kemp⁵ showed that the addition of 1 per cent of phenyl- β -naphthylamine increased from 30 to 125 hours the time required for a mixture to absorb 1 per cent by weight of oxygen at 80° C.

Experiments at the French Rubber Institute have invariably confirmed these results. Moreover it may even be said that the most common application of oxidizability measurements is the study of the comparative effects obtained in the presence and absence of an antioxygenic agent⁶.

There is, however, another and still unrelated fact which points to the possibility of another mode of action, as shown by Dufraisse, Drisch and Pradier-Gibello⁷ in the behavior of litharge, which is ordinarily employed as an accelerator. Continuing the experiments of Tener, Smith and Holt⁸, who found that mixtures containing diphenylguanidine and litharge, respectively, showed the same aging properties when cold, Dufraisse and his collaborators proved on the contrary that litharge makes a vulcanizate much more oxidizable

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 21, No. 1, pages 3-8, January 1944.

and, consequently, that the fixation of a given percentage of oxygen on rubber is less detrimental in the presence of litharge.

Now, as has already been mentioned⁹, it has been observed that there are products, designated as antioxygenic substances, which protect rubber effectively against deterioration by oxygen, yet at the same time have only a slight influence on the rate of absorption of this gas.

This is actually an experimental confirmation of what might be foreseen from the concept of autoxidation, and it proves that, if the antioxygenic substance protects by retarding combination of oxygen, then another protective mechanism enters into play, *viz.*, a diverting of the activity of the peroxides. The existence of this phenomenon seems to be well demonstrated by the experiments to be described in the present paper, which indicate that there are differences between protective agents now recognized only by the single term antioxygenic agents.

COMPARISON OF A SERIES OF ANTIOXYGENIC SUBSTANCES

It was in a systematic study of a series of antioxygenic substances of differing chemical nature that we observed various phenomena which point toward the existence of two modes of action of these substances.

In these experiments a definite rubber mixture was prepared as a control, and this was tested in comparison with other mixtures of the same composition but to which had been added the same percentage of each of the antioxygenic substances being studied. Each of these mixtures was tested, first for its oxidizability, and, secondly for its loss in tensile strength in an artificial accelerated aging test.

The base mixture had the following composition:

Rubber	100
Sulfur	2.5
Benzothiazoyl disulfide	0.25
Tetramethylthiuram disulfide	0.20
Stearic acid	1
Zinc oxide	5
Clay	10

This was vulcanized 8 minutes in moulds at 143° C, which was the optimum cure.

The antioxygenic agents are shown in Table 1. Each was added to the base mixture in the proportion of 1.5 per cent, based on the rubber.

TABLE 1

No.	Chemical composition	Commercial grade
1	β -Naphthol	Antioxygène-BN (Saint-Denis)
2	<i>p</i> -Hydroxybiphenyl	Parazone (du Pont)
3	Aldol- α -naphthylamine	Antioxygène-INC (Saint-Denis)
4	Phenyl- β -naphthylamine	Antioxygène-MC (Saint-Denis)
5	<i>m</i> -Toluylenediamine	Rhône-Poulenc
6	Di- β -naphthyl- <i>p</i> -phenylenediamine	Agerite White (Vanderbilt)
7	Mercaptobenzimidazole	Antiager-MB (I.G. Farbenindustrie)
8	Mixed reaction products of acetone and diphenylamine	BLE (Nauगतuck)
9	Polymerized trimethylhydroquinoline	Agerite Resin-D (Vanderbilt)
10	Hydroquinone	Rhône-Poulenc

It will be noted that the series includes hydroquinone, one of the most "polyvalent" antioxygenic agents, found in the general investigations of Moureu and Dufraisse, and which, according to Dawson¹⁰, is the first antioxygenic sub-

stance which was intentionally used in the rubber industry. However, its use has not become general, contrary to what might have been expected, probably because it disperses rather poorly and, as a result, may cause spots on light colored vulcanizates.

AGING IN THE GEER OVEN

Two series of accelerated aging tests were carried out in the Geer oven, one at 70° C, the other at 80° C. The test-specimens were in the form of dumbbells, with the constricted section 2 mm. wide, cut from sheets approximately 2 mm. thick. The tensile tests were made on a Schopper dynamometer at a speed of 40 cm. per minute. The results are shown in Figures 1 and 2.

Figure 1 gives curves of measurements of the vulcanizates aged at 70° C. Obviously the addition of antioxygenic agents changed the tensile strength of the control mixture, in the sense that in almost all cases the antioxygenic agents increased the tensile strength in the first stages of aging. Strictly speaking it would have been desirable to carry out the tests on a series of samples vulcanized for different lengths of time, but the results obtained were sufficiently well defined to make this unnecessary, and it seemed to be preferable to verify the results merely by repeating the tests.

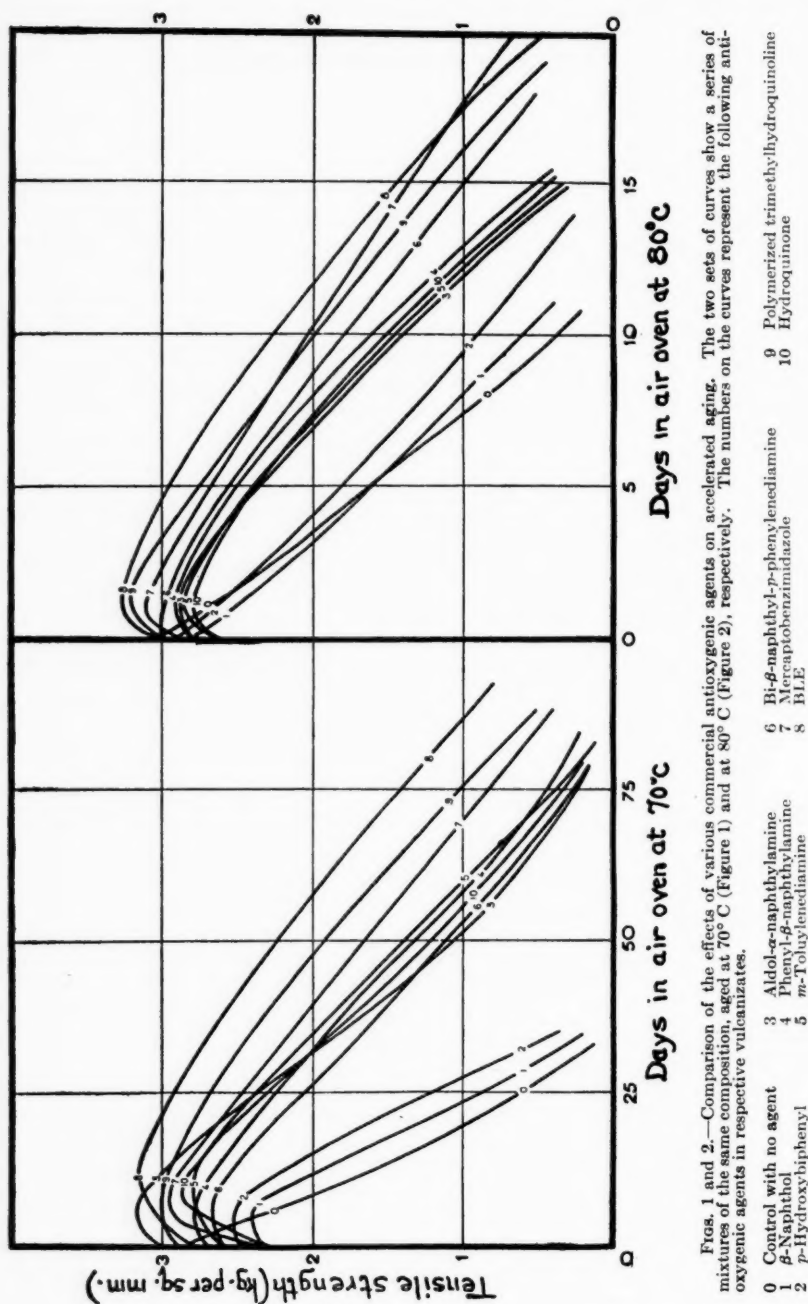
The same mixtures were again prepared and vulcanized under the same conditions. However, this time the aging tests were carried out at 80° C, for two reasons: (1) to shorten the time of the tests, which in the previous series had extended beyond three months, and (2) to operate at the same temperature as that used in making the oxidizability measurements to be sure that this change in temperature had not involved any considerable changes in the order of the aging curves.

The results of the aging tests at 80° C are represented in Figure 2. It will be observed that the original values of the tensile strengths are a little different from those in Figure 1. This is explained by the fact, already mentioned, that the two series of mixtures represented in Figures 1 and 2 were prepared separately, under which conditions differences of this order of magnitude are practically inevitable. It will be seen also that the curves representing aging at 80° C are more closely bunched together than is the group of curves representing aging at 70° C. The higher temperature of the test would seem, then, to reduce the differences between the various vulcanizates. It is interesting to compare this observation with the strictly analogous observation made in connection with the subject of oxidizability¹¹. If one measures the oxidizability of a series of mixtures at different temperatures, the group of curves becomes more closely bunched with increase in temperature. This is a new, indirect proof of the close relation between oxidizability and aging.

Let us examine now, from the graphs, how the various antioxygenic agents studied can be classed according to their protective action. They may be separated into groups.

First of all, curves 1 and 2, which are very close to those of the control sample, show that β -naphthol and *p*-hydroxybiphenyl have only weak antioxygenic power, and therefore confirm what is already known about these compounds¹².

Next comes the compact group of curves 3, 4, 5, 6 and 10, of aldol- α -naphthylamine, phenyl- β -naphthylamine, *m*-toluylenediamine, di- β -naphthyl-*p*-phenyldiamine and hydroquinone, which behave in practically the same way, and are good protective agents. In the tests at 80° C, di- β -naphthyl-*p*-



Figs. 1 and 2.—Comparison of the effects of various commercial antioxygenic agents on accelerated aging. The two sets of curves show a series of mixtures of the same composition, aged at 70°C (Figure 1) and at 80°C (Figure 2), respectively. The numbers on the curves represent the following antioxygenic agents in respective vulcanizates.

0 Control with no agent
1 β -Naphthol
2 *p*-Hydroxybiphenyl
3 Aldol- α -naphthylamine
4 Phenyl- β -naphthylamine
5 *m*-Toluylenediamine
6 Bi- β -naphthyl-*p*-phenylenediamine
7 Mercaptobenzimidazole
8 BLE
9 Polymerized trimethylhydroquinoline
10 Hydroquinone

phenylenediamine appeared to be a little more effective than the other four compounds.

Finally curves 7, 8 and 9 stand out from the rest of the group; in other words, under the conditions of the tests, mercaptobenzimidazole, the mixed reaction product of acetone and diphenylamine (BLE), and trimethylhydroquinoline (Agerite Resin D) impart the best aging properties, with, it would seem, a slight advantage in favor of BLE.

OXIDIZABILITY BY THE MANOMETRIC METHOD

These measurements were made in an atmosphere of oxygen in accordance with the usual technique¹³; each sample was cut into cubes about 2 mm. on a side, and in each case one gram was oxidized at 80° C. The results are shown in Figure 3. They represent the means of several determinations carried out on the two series of mixtures prepared for the accelerated aging tests.

In this series of tests, four groups can be distinguished among the curves obtained.

(1) The control mixture and the mixture containing β -naphthol (curve 1) show practically the same oxidizability.

(2) *p*-Hydroxybiphenyl and mercaptobenzimidazole (curves 2 and 7) reduce the oxidizability by about two-thirds.

(3) *m*-Toluylenediamine, aldol- α -naphthylamine, di- β -naphthyl-*p*-phenyldiamine, and phenyl- β -naphthylamine (curves 5, 3, 6 and 4) reduce the oxidizability to a little more than one-quarter of that of the control sample.

(4) Polymerized trimethylhydroquinoline, hydroquinone, and the mixed reaction product of acetone and diphenylamine (curves 9, 10 and 8) retard most effectively the rate of absorption of O₂; in fact they lowered the rate almost six-fold.

RELATIONS BETWEEN THE PRECEDING DATA

What are the relations between the data obtained from the accelerated aging tests and the oxidizability measurements? To make this comparison easy, the various compounds have been classified in Table 2 according to the

TABLE 2
ORDER OF INCREASING EFFECTIVENESS

Aging in the Geer oven	Oxidizability
Control	Control
β -Naphthol	β -Naphthol
<i>p</i> -Hydroxybiphenyl	<i>p</i> -Hydroxybiphenyl
Aldol- α -naphthylamine	Mercaptobenzimidazole
Di- β -naphthyl- <i>p</i> -phenylenediamine	<i>m</i> -Toluylenediamine
Hydroquinone	Aldol- α -naphthylamine
<i>m</i> -Toluylenediamine	Di- β -naphthyl- <i>p</i> -phenylenediamine
Phenyl- β -naphthylamine	Phenyl- β -naphthylamine
Mercaptobenzimidazole	Polymerized trimethylhydroquinoline
Polymerized trimethylhydroquinoline	Hydroquinone
Reaction product of acetone and diphenylamine	Reaction product of acetone and diphenylamine

increasing improvement which they imparted to aging (based on a loss of tensile strength of approximately 50 per cent) and to the other in which they reduced the oxidizability. The bracketed groups of compounds are those which imparted practically the same properties to the base mixture.

If hydroquinone and mercaptobenzimidazole are excluded, the parallelism between the two lists appears to be excellent. As a matter of fact, the differ-

ences observed between aldol- α -naphthylamine, phenyl- β -naphthylamine, *m*-toluylenediamine and di- β -naphthyl-*p*-phenylenediamine, as far as both oven aging and oxidizability are concerned, are too small to be considered of any significance. The compounds can, then, be classified in the following order of increasing effectiveness:

β -Naphthol

p-Hydroxybiphenyl

Aldol- α -naphthylamine, phenyl- β -naphthylamine, *m*-toluylenediamine, and di- β -naphthyl-*p*-phenylenediamine

Polymerized trimethylhydroquinoline

Reaction product of acetone and diphenylamine

On the other hand, it was found that with hydroquinone the oven aging was poorer than would have been expected from the oxidizability, and, more striking, mercaptobenzimidazole had considerable protective action during oven aging, whereas it reduced the oxidizability relatively little.

This last observation, which, from the point of oxidizability, ranks as equal two antioxygenic compounds of such differing powers as *p*-hydroxybiphenyl and mercaptobenzimidazole, is especially noteworthy. Accordingly no efforts were spared to make certain of its correctness by repeating the mixing and testing several times and by using a glass apparatus without joints so as to avoid all possibility of leakage. All the experiments gave the same result.

It may be concluded, then, contrary to what has been assumed heretofore, that some substances are notably effective in protecting rubber against aging, yet reduce its rate of oxidation to only a slight degree. Such substances must, then, act according to a mechanism which is different from that assumed for true antioxygenic agents.

QUANTITY OF OXYGEN ABSORBED AND DETERIORATION

To show still more clearly the essential differences between the behavior of the two types of agents, experiments were carried out with a view to establishing directly the relation between the quantity of oxygen absorbed and the deterioration of the rubber. For these determinations, there was chosen, in addition to mercaptobenzimidazole, an antioxygenic agent in current use, *viz.*, phenyl- β -naphthylamine, which had just been shown, in the experiments already described, to have an effect on aging comparable to that of mercaptobenzimidazole.

The method used in these experiments was to place the specimens for the dynamometric tests in an atmosphere of oxygen in flasks, allow them to absorb known percentages of oxygen, which were determined by the ascent of the mercury columns in the tubes connected with the flasks, and finally to measure the tensile strengths of the test-specimens oxidized in this way. The operating technique has been described in detail in an earlier paper¹⁴. By this method it is possible to determine the decrease in tensile strength as a function of the percentage of oxygen absorbed.

Figure 4 shows the absorption of oxygen, expressed as percentage of the weight of the rubber as a function of the time of heating at 80° C. It will be seen that, to absorb 1 per cent of oxygen at 80° C, it was necessary to heat the control sample about 56 hours, the sample containing 1.5 per cent mercaptobenzimidazole about 78 hours, and the sample containing 1.5 per cent phenyl- β -naphthylamine about 172 hours. This confirms the results obtained in the manometric measurements shown in Figure 3.

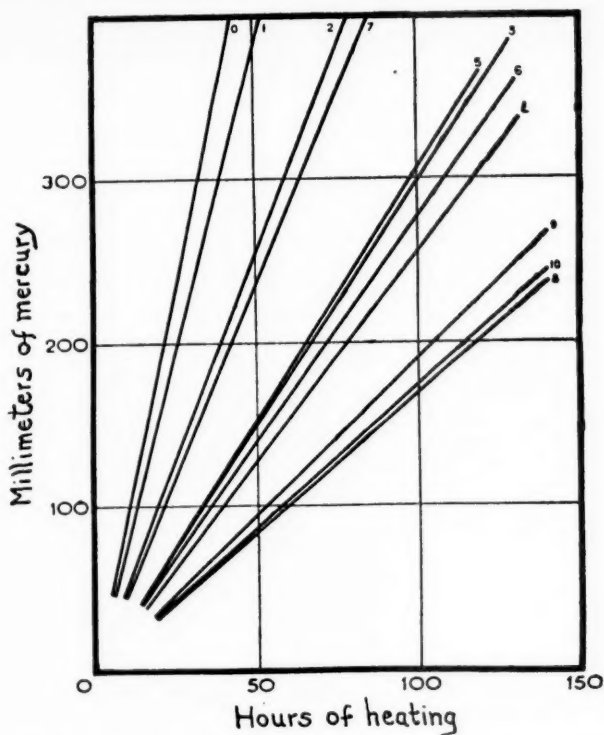


FIG. 3.—Comparison of oxidizability at 80° C of mixtures containing various commercial antioxygenic agents. The numbers on the curves represent the same mixtures shown in Figures 1 and 2.

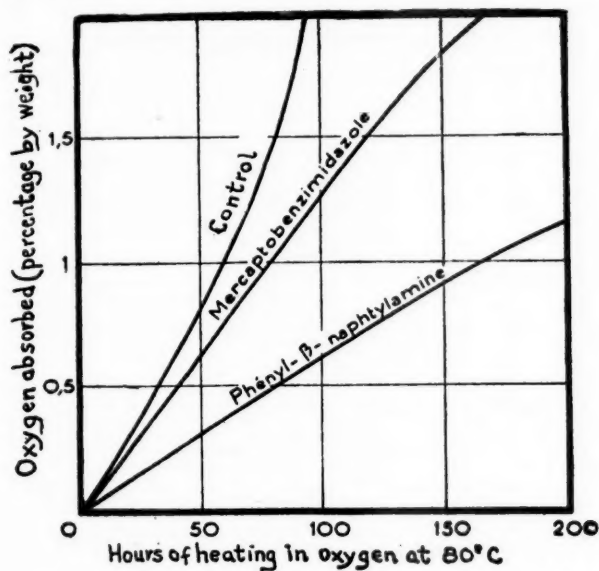


FIG. 4.—Influence of different types of protective agents on the absorption of oxygen.

In each series of experiments, the flasks were opened after approximately 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.5, and 2.0 per cent, respectively, of oxygen had been absorbed. The samples were then removed and their tensile strengths measured.

At the same time, a parallel series of samples was heated under the same conditions but in a vacuum. By determining the tensile strengths of this series of samples, it was possible to judge the changes in tensile strength resulting from heat alone. During the early stage of deterioration, there was actually an increase in the tensile strength. By correlating the two series of measurements, it was possible to evaluate the losses in tensile strength actually brought about by the oxygen itself.

Table 3 shows representative measurements of the mixture protected by mercaptobenzimidazole.

TABLE 3

Hours of heating at 80° C	Oxygen absorbed (percentage by weight)	Tensile strength		Loss (percentage)
		Heated in vacuum (kg. per sq. cm.)	Heated in oxygen (kg. per sq. cm.)	
0	0	241	241	0
12	0.20	263	261	0.9
38	0.40	263	252	4.0
60	0.77	242	205	15.2
90	1.15	244	136	44
164	2.0	244	78	68

Figure 5 shows the curves representing the three mixtures studied. They are particularly characteristic between 0 and 0.6 per cent of absorbed oxygen. Above this absorption, the changes become too deep-seated, and the measure-

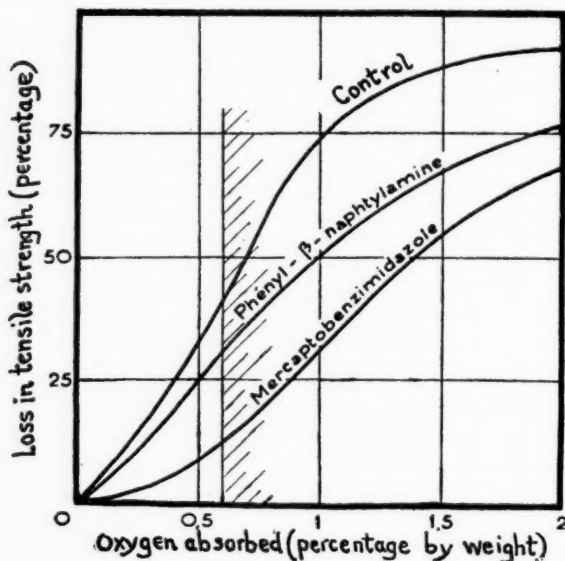


FIG. 5.—Loss in mechanical properties as a function of the oxygen absorbed. With an absorption above 0.6 per cent by weight, secondary phenomena enter to mask the very characteristic trend of the curves.

ments may become complicated by secondary phenomena, *e.g.*, the progressive disappearance of the antioxygenic agent. It will be noted that, with phenyl- β -naphthylamine, the absorption of a definite percentage of oxygen brings about practically the same deterioration as that of the control sample. On the contrary, with mercaptobenzimidazole, the absorbed oxygen is manifestly much more detrimental. At an absorption of 0.4 per cent, for example, the loss of tensile strength of the control sample was about 25 per cent, that of the mixture containing phenyl- β -naphthylamine about 20 per cent, and that of the mixture containing mercaptobenzimidazole only about 5 per cent.

The harmful effect of oxygen depends, therefore, to a considerable degree on the nature of the protective agent in the mixture.

The effort will next be made to explain the reasons for these differences in behavior by considering the mechanisms according to which the products may react.

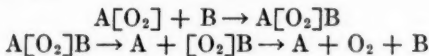
THEORY OF THE MECHANISM OF THE OBSERVED REACTIONS

If the rubber molecule is represented by A, it is possible, as has already been done¹⁵, to explain the oxido-transformation which it undergoes by the intermediate formation of a primary peroxide:



This peroxide then decomposes, liberating its oxygen, at the same time causing scission of the rubber molecule at the point where the oxygen had been fixed. The liberated oxygen is capable of combining again with another molecule of rubber. This is, then, the beginning of a chain of reactions which continues indefinitely and is limited only by the transformation of the primary peroxide into a stable form, whereby the oxygen loses its reactivity. This chain of reactions leads to the complete deterioration of the rubber, which, as may be easily realized, appears to bear no relation to the small percentage of oxygen absorbed.

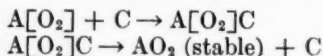
Let us next consider the behavior of an inhibitor which manifests its activity in its ability both to decrease the rate of oxidation and to improve the aging properties, *i.e.*, what may be called a typical antioxygenic agent. This agent B has the ability, in accordance with the normal mechanism of antioxygenic action¹⁶, to hinder the combination of oxygen with rubber. It may be assumed that it combines with the peroxide and that the resulting product then decomposes, with liberation of the constituents unaltered, thus:



The net result of this is, therefore, as if the agent B protects the rubber molecule against attack by oxygen and, within the extent of its power, acts as a barrier to this oxygen. From a practical point of view this power is limited; part of the oxygen escapes this barrier of B, and the peroxide completes its work of destruction. However, the intervention of B at least has the effect of retarding this ultimate destruction.

How can one reconcile these theories with the action of an inhibitor C which, like mercaptobenzimidazole, is very effective in protecting against physical deterioration, yet has hardly any influence on the rate of oxidation? They can be reconciled in a very simple way, it would seem, by assuming that, as in

the case of agent B, C combines with the peroxide, but that the decomposition of this compound yields this time, in addition to unaltered C, an oxide of rubber:



or



The effect of the inhibitor C is, therefore, to force the oxygen to form a simple oxide instead of an active peroxide capable of bringing about complete destruction of the molecule. The inhibitor in some way deactivates the peroxide, and it may consequently be classed as an *antioxygenic deactivator*.

As oxygen continues to combine with the rubber, the action of a product of this character leads to the progressive replacement of the rubber by an oxide, which can be regarded as an inert filler, and a relatively large proportion of which is accordingly required to bring about any considerable change in the mechanical properties of the rubber. It is no longer a question of an oxidation transformation, but of simple oxidation, comparable for example to the transformation of benzaldehyde into benzoic acid. As a matter of fact, just as agent B fails to inhibit the action completely, likewise a part of the peroxides which are formed escape the action of the deactivator. In effect, therefore, agent B and agent C have the same influence on aging, despite the fact that their protective action depends on different mechanisms.

It should be mentioned, in addition, that these different mechanisms represent two ideal classes of protective agents. As far as incipient oxidation¹⁷ is concerned, it may be said that with typical antioxygenic substances the changes are the same as when no antioxygenic substance at all is present, and with deactivators the changes are inappreciable, at least theoretically. However, in practice every substance which has antioxygenic properties appears to function by a combination of the two mechanisms, with one or the other mechanism more or less predominating. An examination of Figure 5 will show that the closer the curve of a compound is to the abscissa, the greater the deactivating effect of the compound, and the closer the curve of a compound is to that of the control vulcanizate, the greater are the normal antioxygenic characteristics of the compound.

It is now easy to understand why the classification which is based on the aging properties does not conform exactly to the order of oxidizability. Mercaptobenzimidazole, which has a definite deactivating power, allows oxygen to combine without greatly reducing the rate of fixation, but orients it in the direction of the formation of inert oxides. Hydroquinone, with normal antioxygenic power, is distinguished on the one hand from polymerized trimethylhydroquinoline (Agerite Resin D) and the reaction product of acetone and diphenylamine by its weaker antioxygenic power (permitting for a given percentage of fixed oxygen the formation of a greater proportion of peroxides), and, on the other hand, from the aldol- α -naphthylamine, *m*-toluenediamine, di- β -naphthyl-*p*-phenylenediamine, phenyl- β -naphthylamine group by its lower deactivating power, whereby from the point of view of the ultimate deterioration for a given percentage of fixed oxygen, the greater deactivating power of these last compounds counterbalances their lower antioxygenic power.

It is possible to explain in the same way the action of litharge on the assumption that it has a certain amount of deactivating power.

Finally it will be realized that the harmful percentages of oxygen found by different investigators have differed to a certain extent, according to the nature

of the ingredients in the mixtures and the more or less complex mechanism of their action.

OXIDIZABILITY AND PROTECTIVE POWER

The facts and discussion above confirm in another way the assertion, which has been made many times, that oxidizability is not in itself sufficient to serve as a measure of the protective power of a substance. However, to avoid any mistake in understanding this property, it seems advisable to review again, though briefly, the principles which govern the use of the manometric method and the kind of information which may be expected to be obtained from it.

The manometer is a practical and rapid apparatus¹⁸, and above all is adapted to control work. The oxidizability of a mixture, like its density, for example, is a physical constant¹⁹, and is more or less influenced by every change in composition. However, it is necessary to be careful in interpreting correctly the direct results of any such measurements.

For example, whenever the addition of a new ingredient to a mixture results in reduced oxidizability, there can be no mistake about what happens; there is a corresponding improvement in aging properties. When, on the contrary, a negative result is obtained, measurement of the oxidizability alone is not sufficient to judge quality, for a deactivating effect may be involved, and the fact that the rate of oxidation is not reduced does not necessarily mean that there is no protective action.

It should be noted, however, that the great majority of antioxygenic agents for rubber which are now known show their effects by reducing the oxidizability of rubber. With the manometer it is possible to determine the effectiveness of each of these products by working with small samples and for a short time. However, it is obvious that the method must not be expected to furnish a direct means of comparison of the protective powers of two different antioxygenic agents, since, as has already been seen, the agent which reduces the oxidizability the most is not necessarily the same agent which gives the best protection against aging.

In applying the manometric method to the examination of agents capable of retarding the deterioration of rubber by oxygen, care must be taken not to draw too hasty conclusions. The method gives reliable information concerning the effects of an agent having normal antioxygenic power, but it must be supplemented by an aging test (artificial or, *a fortiori*, natural) if the agent has any deactivating power.

On the other hand, the present work is one more proof of the value of the manometric method as a means of investigation. With its aid it is possible to obtain new data the interpretation of which will always, as far as future progress is concerned, carry more weight than theoretical concepts which are based on more or less complex equations, such as those which have been derived by some authors²⁰, but which are not yet supported by a sufficient number of well established facts. In the present case, the manometric method has made it possible for the first time to bring to light a phenomenon which otherwise would not have been known, since the retarding action of antioxygenic substances on the absorption of oxygen has seemed to be a well established fact, and which would not, *a priori*, suggest the existence of any other mechanism of protection. Only by the use of the manometer is it possible to distinguish, among all protective agents, those which have an antioxygenic action or a deactivating action, and thereby to combine them rationally in such a way as to increase their effectiveness.

CONCLUSIONS

The observations which are recorded in the present paper represent an extension of the single case of litharge which has already been described. They show that, when small percentages of certain substances are added to rubber with a view to protecting the rubber from deterioration by oxygen, these substances are capable of directing the combination of oxygen with the rubber in different ways. This is shown by the fact that, as a result, a given percentage of combined oxygen does not lead to the same deterioration in physical properties.

This difference in behavior can be explained logically on the basis of the antioxygenic theory by assuming that some agents act, not by retarding the rate of oxidation, but by deactivating the peroxides as soon as they are formed.

By what term are these agents to be designated? First of all it should be recalled how an antioxygenic substance is defined²¹. Every substance is an antioxygenic agent when it has the power, in small percentages, of retarding the rate of absorption of free oxygen by an autoxidizable substance. This definition obviously does not apply to a perfect deactivating agent, since the latter has no effect on the rate of absorption of oxygen, in spite of it too protecting rubber against deterioration by oxygen, and therefore being equally worthy, from the practical point of view, of being called an antioxygenic agent. However, this would only lead to confusion between the phenomenon itself and its effects.

Furthermore, since commercial antioxygenic substances appear to show, to a greater or less degree, a combination of the two actions, one might consider designating them by some term which would embody both mechanisms. The word "antiaging agent" is not suitable, for it is too general and applies to cases where, in addition to oxygen, other influences such as light and repeated flexing play a part. There is, then, a problem in terminology to be settled, but this will have to be left unanswered provisionally until sufficient facts which have a more direct bearing on the case are available.

Finally attention should be called to the useful effect which may be pictured as a possibility when the two types of protective agents which have been described act jointly. In other words, if the two mechanisms in question were to be superimposed, it would appear to be possible to improve considerably the resistance of rubber to deterioration by oxygen, since any oxygen which escapes the protective action of the true antioxygenic agent has its harmful effect reduced by the deactivating agent. To express it figuratively, it might be said that oxygen which has succeeded in overcoming the first obstacle opposing its action finds itself confronted with a new defense which puts the oxygen partially out of action. As shown by experiments carried out on this subject, which are described in the following paper of this series, this theoretical conclusion is actually borne out by the results of the experiments.

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II. COMBINATION OF THE TWO MODES OF ACTION *

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INTRODUCTION

In the preceding paper, one of the present authors has shown that, by the incorporation of small percentages of certain substances into rubber for the purpose of protecting it against deterioration by oxygen, combination of oxygen with rubber may proceed in different ways. Apart from antioxygenic agents, which retard the rate of oxidation, some substances appear to have the effect of deactivating the peroxides. An examination of the two mechanisms in question might lead to the conclusion that, theoretically, their joint effect would result in a notable increase in the resistance to deterioration by oxygen. This is, in fact, what is found to be true as a result of experiments which are to be described.

Various investigators have already recommended, particularly in the patent literature, the use of mixtures of antioxygenic agents. However, in this case the phenomena involved are quite different from the phenomenon concerned in the present work, in that they most often involve combinations of agents which influence, on the one hand, the effect of oxygen and, on the other hand, deterioration by some other factor, *e.g.*, heat or repeated flexing.

In 1929, for instance, Calcott, Douglass, Hayden and E. I. du Pont de Nemours Co.¹ patented the use of combinations of chemical substances which retard deterioration brought about by heat and oxygen, in which case each of the compounds is especially adapted to the prevention of a definite type of deterioration. The products indicated are, on the one hand, aromatic secondary amines, *e.g.*, phenyl- α -naphthylamine, which are very good inhibitors of oxidation, and, on the other hand, aromatic diamino compounds, *e.g.*, *m*-toluyl-enediamine, which impart exceptional resistance to heat.

Other investigators have been preoccupied more particularly with flex-cracking, pointing out that there is no simple relation between resistance to deterioration (static oxidation) and resistance to fatigue (dynamic oxidation). Somerville, assuming that the oxygen in rubber plays some part other than that of atmospheric oxygen, proposed completing the action of an antioxygenic substance by that of an organic absorber of oxygen capable of eliminating the oxygen originally present in rubber. From this came a series of patents, taken out by the R. T. Vanderbilt Company, dealing with the simultaneous use of catalytic antioxygenic substances (aromatic secondary amines, reaction products of aromatic amines with aldehydes or ketones), and organic reducing agents, such as pyrogallol² and hydroxyhydroquinone³. Somerville has given in detail the results of these investigations in one of the few scientific papers on this subject which have been published⁴.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 21, pages 89-93, May 1944.

Baird, Goldstein and Jones⁵ likewise have patented combinations of phenyl-naphthylamines and quinoline derivatives aimed at simultaneous protection against normal aging and flex-cracking. The inventors themselves point out, however, that these mixtures do not increase resistance to normal deterioration by oxygen. Somerville, for instance, states that aging in the oxygen bomb is not altered, and Jones and his collaborators that the aging properties remain unchanged.

Again to retard fatigue and cracking, the United States Rubber Company recommends⁶ the addition to aromatic secondary amines of triaryl derivatives of certain elements of the fifth group, notably triphenylstibine. The results which are described are concerned only with flexing tests.

Finally there should be mentioned in this same connection the patents of Semon⁷, Sibley⁸ and Howland⁹, the basis of which consists primarily of "activating" certain types of antioxygenic agents by the joint action of diphenyl-*p*-phenylenediamine. With respect to aging in the Bierer-Davis bomb or the Geer oven, an examination of the data which are presented do not give evidence of any practical improvement.

On the other hand, the combined use of the two protective mechanisms just described is concerned primarily with degradation by oxygen, and is evident in increased resistance to aging of the rubber mixtures in ordinary artificial tests¹⁰, irrespective of any effects which this combination may have on other evidences of deterioration.

COMBINED USE OF AN ANTIOXYGENIC AGENT AND A DEACTIVATING AGENT

With a view to ascertaining whether these theoretical views can be confirmed experimentally, two compounds were chosen for study which had been utilized previously for showing differences in the relation between the percentage of oxygen absorbed and the extent to which rubber deteriorates, *viz.*, phenyl- β -naphthylamine and mercaptobenzimidazole, the first of which is a typical antioxygenic agent, the second of which is a deactivating agent.

The mixture employed in the previous experiments, which contained in parts by weight: rubber 100, sulfur 2.5, tetramethylthiuram disulfide 0.20, benzothiazoyl disulfide 0.25, stearic acid 1, zinc oxide 5, and clay 10, and which will be designated as mixture no. 1, was chosen again. It was vulcanized 8 minutes in moulds at 143° C, and was compared with corresponding mixtures to which had been added:

(1) Phenyl- β -naphthylamine	2 parts
(2) Mercaptobenzimidazole	2 parts
(3) Phenyl- β -naphthylamine	1 part
Mercaptobenzimidazole	1 part

Figure 1 shows the changes in the tensile strength by aging in a Geer oven at 70° C; Table 1 gives some of the corresponding values calculated in terms of percentage losses in tensile strength.

It is seen that the improvement in resistance to oxygen is very marked; after aging for 38 days, the loss in tensile strength of the vulcanizate containing phenyl- β -naphthylamine was 52 per cent, and the loss in the vulcanizate containing mercaptobenzimidazole was 33 per cent, whereas the loss in the vulcanizate containing both phenyl- β -naphthylamine and mercaptobenzimidazole was only 6.8 per cent.

A control series of tests of mixtures of the same compositions, prepared a second time, and aged naturally under the same conditions, gave practically the same results; after an equivalent period of aging the losses in tensile strength were 51, 33 and 6 per cent, respectively.

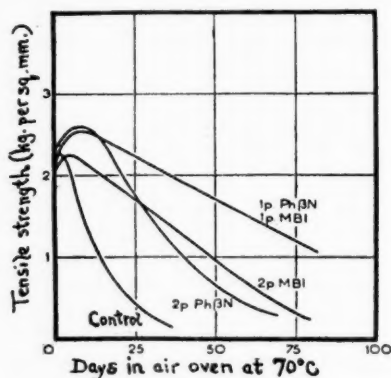


Fig. 1.—Effects of the combined use of an antioxygenic agent and a deactivating agent.

TABLE 1

Percentage loss in tensile strength

Days of aging in air oven at 70° C	Control	Phenyl-β-naphthylamine (2 parts)	Mercapto-benzimidazole (2 parts)	Phenyl-β-naphthylamine (1 part) mercapto-benzimidazole (1 part)
5	-10	+8.9	+8.1	+9.8
17	-64	-2.4	-5	+6.1
38	-94	-52	-33	-6.8
50	—	-72	-54	-17
70	—	-90	-83	-39

INFLUENCE OF DIFFERENT PROPORTIONS OF THE TWO PROTECTIVE AGENTS

To demonstrate more clearly the results described above, the effects of 2 parts of each of the two agents in question were compared with the effect of 1 part of these two agents. But since the theory assumes that the two mechanisms in question act jointly, and on the other hand, that the use of 1 part of each agent does not necessarily give the optimum protective effect, it might be expected that higher proportions would give still better results. Actual tests showed that this is so. The following proportions were used, and the results are shown in Figure 2.

Phenyl-β-naphthylamine	1	2	1	2
Mercaptobenzimidazole	1	1	2	2

It should be noted that the tensile strength of the vulcanizate containing 1 part of each agent diminished from 2.7 to 2 kg. per sq. mm. when aged 50 days in the Geer oven, whereas the tensile strength of the vulcanizate containing 2 parts of each agent diminished from 2.7 to 2 kg. per sq. mm. only after 80 days in the Geer oven.

These preliminary tests naturally should be completed by a systematic series of experiments on the total percentage and the proportion of the two agents which give the best aging, basing the results on the optimum percentage of each of the agents when used separately.

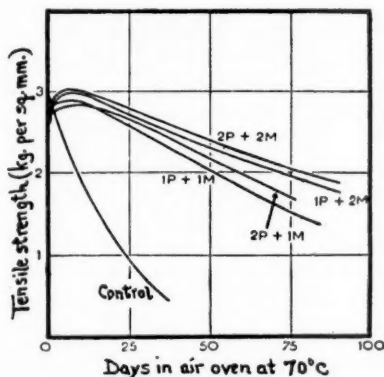


FIG. 2.—Influence of the various percentages of phenyl- β -naphthylamine (P) and of mercaptobenzimidazole (M). The figures accompanying the designations M and P are the parts by weight per 100 parts of rubber.

INFLUENCE OF THE NATURE OF THE VULCANIZING SYSTEM

The ease with which the catalytic power can reverse itself in autoxidation reactions is already well known, and Dufraisse has called attention many times to this phenomenon¹¹. Pelizzola has, for example, described the case of pyrogallol¹², which either retards or accelerates the deterioration of rubber according to whether zinc oxide or an organic accelerator is absent or present.

There is no reason, therefore, for being surprised at the following observation, which was made in the course of other experiments. Mercaptobenzimidazole, which behaves as a very good protective agent in mixture no. 1 is, on the contrary, ineffective, or even deleterious in a simple rubber-sulfur mixture. This made it important to find out whether, in changing the nature of the vulcanizing system, we had by chance encountered a typical instance of this phenomenon.

Accordingly, a series of mixtures were prepared with different accelerators, the compositions of which are shown in Table 2.

TABLE 2

Ingredient	100	100	100	100
Rubber				
Sulfur	3.5	3	2	3
Mercaptobenzothiazole	0.75	—	—	—
Diphenylguanidine	—	1	—	—
Tetramethylthiuram disulfide	—	—	0.3	—
Benzothiazoyl disulfide	—	—	—	1
Stearic acid	0.5	2	1	1
Zinc oxide	6	10	5	5
Clay (kaolin)	10	—	10	10
Time (min. of vulcanization at 143° C)	75	60	10	20

Four samples from each of these base mixtures were prepared and vulcanized:

- (1) the base mixture without any added agent;
- (2) phenyl- β -naphthylamine, 2 parts;
- (3) mercaptobenzimidazole 2 parts;
- (4) phenyl- β -naphthylamine, 1 part + mercaptobenzimidazole 1 part.

Figure 3 shows the results obtained in the Geer oven aging tests. The simultaneous use of an antioxygenic agent and a deactivating agent led in all cases to an improvement in the resistance to oxygen. However, the intensity of this effect depends on the nature of the accelerator; *e.g.*, the effect was marked with mercaptobenzothiazole, and was relatively small with diphenylguanidine. The explanation of these differences in behavior offers an interesting problem for study.

INFLUENCE OF THE TIME OF VULCANIZATION

Since the addition of ingredients such as the protective agents used in the present work had in all cases a more or less marked effect on the rate of vulcanization, it seemed well to examine to what extent changes of this kind might affect the course of the aging curves and, although it seemed rather improbable, whether the changes in aging properties were not simply attributable to under-vulcanization.

A new series of tests was therefore carried out with mixture no. 1 through a wide range of cures, *viz.*, 8, 15, 30 and 60 minutes, that is, a range which extends well beyond the optimum cure¹³. A comparison of the sixteen aging curves obtained shows that those with the least rapid descent represent the combination of the two protective effects. However, since these curves start between 1.5 and 2.5 kg. per sq. mm. and show numerous intersections, they form too confused a grouping to make it possible to represent them all clearly on a graph of small dimensions. It seemed preferable for the sake of clarity and ease of interpretation simply to give enough of the results to show the general trend of the curves.

It is at a point where the deterioration corresponds to a loss of about 50 per cent of the original tensile strength that differences between the individual mixtures commenced to be well defined. Accordingly Table 3 shows the num-

TABLE 3

Time of vulcanization (min.)	Control mixture no. 1	Days of oven aging for the tensile strength to be 1 kg. per sq. mm.		
		Phenyl- β -naphthylamine (2 parts)	Mercaptobenzimidazole (2 parts)	Phenyl- β -naphthylamine (1 part) + mercaptobenzimidazole (1 part)
8	27	47	76	110
15	21	41	61	100
30	20	34	57	90
60	21	26	58	82

ber of days in the Geer oven which is necessary for each sample to deteriorate to such an extent that its tensile strength is only 1 kg. per sq. mm.

The data in Table 3 need no comment, and show that the mixtures which were protected by a combination of phenyl- β -naphthylamine and mercaptobenzimidazole had the best aging properties, irrespective of the state of vulcanization.

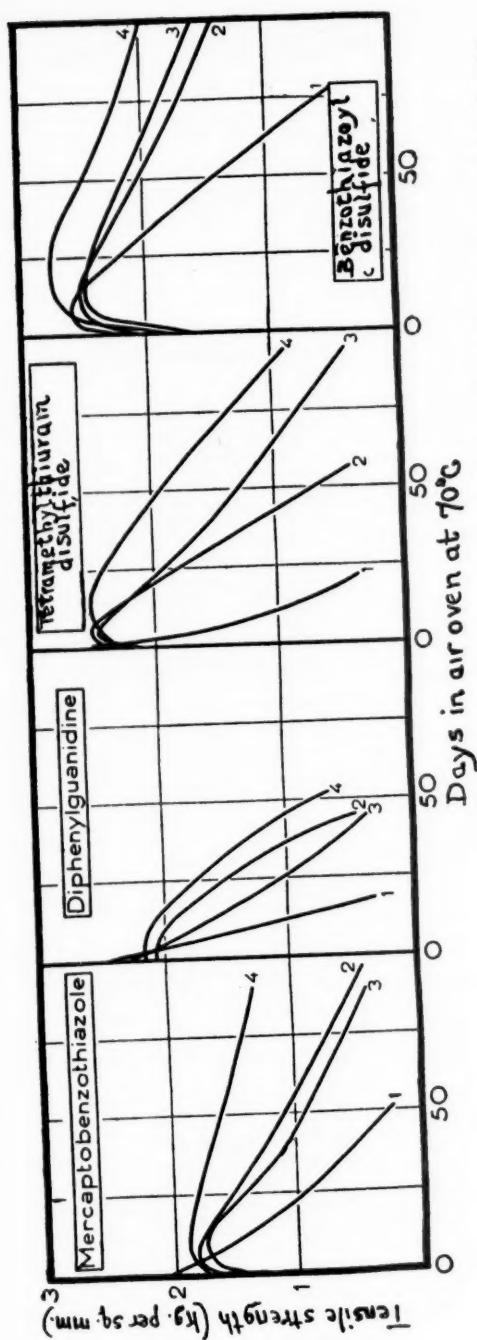


FIG. 3.—Tests with different accelerators. The curves marked 1 represent the control vulcanizates; those marked 2, vulcanizates containing phenyl- β -naphthylamine; those marked 3, vulcanizates containing mercaptobenzimidazole, and those marked 4, vulcanizates containing the mixture of phenyl- β -naphthylamine and mercaptobenzimidazole.

A similar experiment was carried out with mixture no. 2, accelerated by mercaptobenzothiazole, which was vulcanized for 75, 100, 125, and 150 minutes. The results were quite similar to the preceding ones. After the initial period, where the results are a little confused because the tensile strengths increase and the curves intersect, the groups of curves representing each vulcanizate separate clearly. The mean times of aging required to lower the tensile strength 50 per cent are 26 days for the control vulcanizate, 58 days for the vulcanizate containing mercaptobenzimidazole, 72 days for the vulcanizate containing phenyl- β -naphthylamine, and 116 days for the vulcanizate containing a combination of these two protective agents.

COMPARISON WITH VARIOUS MIXTURES OF ANTIOXYGENIC SUBSTANCES

Two more points likewise seemed of interest. On the one hand it seemed interesting to compare the activity of the combination of antioxygenic agent and deactivating agent with the activities of various commercial mixtures of antioxygenic substances which have been highly recommended. On the other hand it seemed of interest to ascertain whether the protective effect of the deactivating agent is evident with normal antioxygenic agents other than phenyl- β -naphthylamine, since the latter was chosen merely by chance in the original experiments.

To this end, a series of comparative experiments was carried out, by adding to mixture no. 1 (vulcanized 8 minutes at 143° C) various combinations (2 parts by weight per 100 parts of rubber) and aging the vulcanizates in the Geer oven and in the Bierer-Davis oxygen bomb.

Table 4 shows, by the letters designating the particular agents employed, the compositions of the latter and, where possible, their commercial names.

TABLE 4

Designation	Trade name	Composition	
A	Neozone (standard)	Phenyl- α -naphthylamine	50%
		<i>m</i> -Toluylenediamine	25%
		Stearic acid	25%
B	Neozone-E	Phenyl- β -naphthylamine	75%
		<i>m</i> -Toluylenediamine	25%
C	—	Neozone-E	50%
		Mercaptobenzimidazole	50%
D	Thermoflex-A	Phenyl- β -naphthylamine	50%
		Di- <i>p</i> -methoxydiphenylamine	25%
		Diphenyl- <i>p</i> -phenylenediamine	25%
E	BLE	Reaction products of acetone and diphenylamine	50%
F	—	BLE	50%
		Mercaptobenzimidazole	50%
G	—	Phenyl- β -naphthylamine	
		Phenyl- β -naphthylamine	50%
H	—	Mercaptobenzimidazole	50%
J	Arkoflex-C	Phenyl- α -naphthylamine	65%
		Diphenyl- <i>p</i> -phenylenediamine	35%
K	—	Litharge	
L	—	Phenyl- β -naphthylamine	50%
		Litharge	50%

The results obtained with the various agents listed in Table 4 are condensed in Table 5 and, in the case of the Geer oven aging tests, in Figures 4 and 5.

TABLE 5
PERCENTAGE LOSS IN TENSILE STRENGTH BY AGING IN AIR AT 70° C
AND IN OXYGEN UNDER 21 KG. PER SQ. MM.
PRESSURE AT 60° C FOR VARIOUS TIMES

Protective Agent	Aging in air (days)				Aging in oxygen under pressure (days)			
	12	33	45	54	7	14	21	35
A	17	43	63	86	18	31	46	70
B	15	51	75	89	10	27	41	61
C	2	26	34	43	not determined			
D	11	41	58	70	10	26	38	57
E	12	36	56	66	10	21	33	62
F	2	18	27	30	4	8	19	34
G	6	43	58	82	8	10	20	50
H	5	23	31	35	2	5	14	26
J	3	49	83	89	3	19	12	62
K	(4)	49	75	87				
L	4	30	45	62				
control	22	87	93	—	14	38	72	86

The results shown in Table 5 and in Figures 4 and 5 lead to the following conclusions.

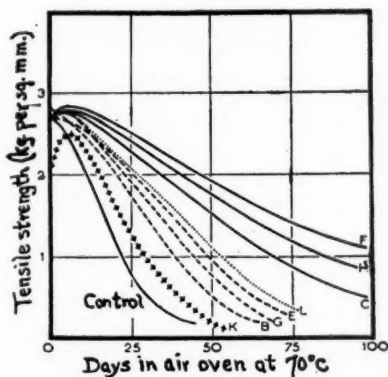


FIG. 4.—Combination of a deactivating agent and various antioxygenic agents. Table 4 shows the meaning of the letters on the curves.

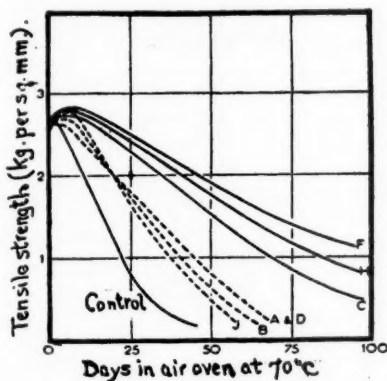


FIG. 5.—Comparison of mixtures of antioxygenic agents with combinations of antioxygenic agent and deactivating agent. Table 4 shows the meaning of the letters on the curves.

(1) When an ordinary antioxygenic substance, such as Neozone-E, BLE or phenyl- β -naphthylamine, is replaced by a mixture of one of these antioxygenic substances and a deactivating agent, *e.g.*, mercaptobenzimidazole, there is always an improvement in aging. This can be seen in Figure 4, where curves C, H and F are located considerably above the corresponding curves B, G and E representing mixtures containing only an antioxygenic agent.

(2) The commercial mixtures which were tested, *viz.*, standard Neozone, Neozone-E, Akroflex-C, and Thermoflex-A. impart aging properties quite similar to those obtained with simple antioxygenic agents such as phenyl- β -naphthylamine and BLE. This fact confirms what was pointed out in the introduction, *viz.*, that the commercial mixtures improve resistance to flex-cracking without having any particular effect on normal aging. Figure 5 shows the difference indicated between the corresponding aging curves; first, for these mixtures (curves A, B, D, J); secondly for combinations of antioxygenic and deactivating agents (curves C, F, H).

(3) As might be expected from the experiments of Dufraisse and his collaborators¹⁴, as mentioned in the first part of this work, litharge shows a certain deactivating power. It can, in fact, be shown that the addition of 2 parts of litharge improves only slightly the aging properties (curve K in Figure 4); so might not even this increase in resistance to deterioration be attributed merely to the rather marked state of undercure of the mixture? On the contrary, the combination of 1 part of phenyl- β -naphthylamine and 1 part of litharge (curve L) proved itself superior to phenyl- β -naphthylamine (curve G).

Although the aging tests in the Bierer-Davis oxygen bomb were not carried out on all the mixtures tested in the Geer oven, they do warrant the same conclusions (see Table 5). Here too the combinations of antioxygenic agent and deactivating agent (compounds F and H) gave the best protection.

VARIATION IN THE OXIDIZABILITY

Finally it is proper to ask in what way the oxidizability of mixtures varies according to the character of the protective agent used. It might be assumed, *a priori*, that the oxidizability of a sample containing a combination of an antioxygenic agent and deactivating agent would be intermediate between the oxidizability of the mixture containing the antioxygenic agent and the oxidizability of the mixture containing the deactivating agent. However, this is not what was actually found to be true, for it was observed, in every case examined in the present work, that the oxidizability was less than that of the mixture containing the antioxygenic agent.

Some of the experimental results are shown in Table 6.

TABLE 6
HOURS OF OXIDATION IN THE MANOMETER, 80° C, REQUIRED FOR THE
MERCURY COLUMN TO ASCEND 200 MM.

Mixture no.	Control (no protective agent)	With mercaptobenzimidazole (2 parts)	With phenyl- β -naphthylamine (2 parts)	With phenyl- β -naphthylamine (1 part) + mercaptobenzimidazole (1 part)
1	20	29	60	70
2	18	29	46	56
3	10	21	41	45
4	11	18	56	75
5	29	56	82	106

These results would seem to indicate that the contribution of the deactivating agent is to reinforce the antioxygenic power of the antioxygenic agent.

This may mean that there is a change in the mechanism of the protective action of the antioxygenic agent. This problem justified a thorough study because of the light it might throw on the complicated phenomena involved in protection against oxygen.

CONCLUSIONS

The various experiments described in the present paper show that the combined use of an antioxygenic agent and a deactivating agent makes it possible to improve the aging of rubber mixtures to a considerable extent. This is, then, an experimental confirmation of the hypothesis which had previously been advanced as a result of observations on the relation between oxidizability and aging.

It should be pointed out here that the present work is concerned only with static aging, with oxygen as the only factor playing any part in the deterioration occurring in ordinary artificial aging tests. In dynamic aging, other factors undoubtedly play a part, but it is true, none the less, that the action of oxygen is still of prime importance, as has been very clearly shown by Neal and Northam¹⁵. The improved aging which was observed in the present work should, then, play a part in dynamic aging, and this has been confirmed by preliminary tests, the progress of which cannot be reported at this time.

From another point of view, the differences in behavior which seemed to depend on the character of the vulcanizing system, confirm the fact that, even when only static aging is concerned, antioxygenic agents cannot always be rated in the same order. It is, therefore, advisable, as is done in choosing the accelerator, to make a judicious choice of protective agent or combination of protective agents for each rubber mixture, taking care to avoid any general rules which have not been previously checked.

Finally, the behavior of mercaptobenzimidazole and of litharge should be an inducement to study other compounds which might be deactivating agents, particularly imidazoles, thiazoles, and oxazoles, in an effort to find products having the greatest possible deactivating power. By the use of a manometer it will be possible to choose, among protective agents against oxygen, those which react in accordance with this mechanism. It will then be possible to proceed systematically in combining these protective agents with normal antioxygenic agents.

Such a method of investigation of the improvement of aging offers, therefore, a means of avoiding, at least in part, the empiricism which now prevails in this field, and to formulate on a rational basis mixtures of protective agents having a high degree of effectiveness.

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- ¹³ It should be recorded that, in spite of this, all the protected mixtures, whatever their state of vulcanization, showed an increase in tensile strength during the initial stage of aging.
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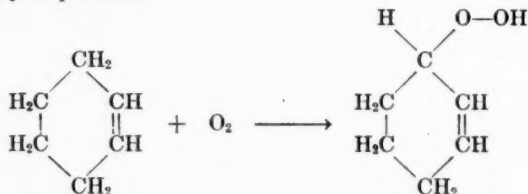
THE AUTOXIDATION OF RUBBER AND MECHANISMS OF PROTECTION AGAINST OXYGEN *

JEAN LE BRAS

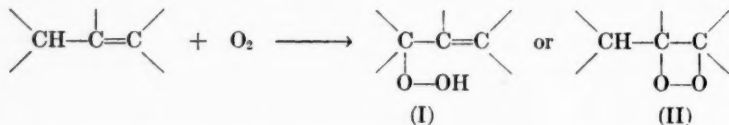
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INTRODUCTION

The autoxidation of ethylenic hydrocarbons has been the object of various investigations, and various authors, among whom Engler¹ and Stephens² in particular might be mentioned, have studied the part played by peroxides. Up to 1936 it was generally believed that structurally these peroxides represent the fixation of one molecule of oxygen on the double bond. About this time, however, Criegee³ on the one hand, and Hock and Schrader⁴ on the other, published papers almost simultaneously on the preparation and constitution of cyclohexene peroxide, in which they demonstrated that the latter can exist in the form of a hydroperoxide.



Later these investigators offered further proof in favor of this view by extending the reaction to other hydrocarbons⁵. These studies led to the important conclusion that ethylenic hydrocarbons have two sensitive points: the double bond itself, and the carbon in α -position to this double bond; hence there are two forms of the peroxide, the first of which retains its unsaturated character.



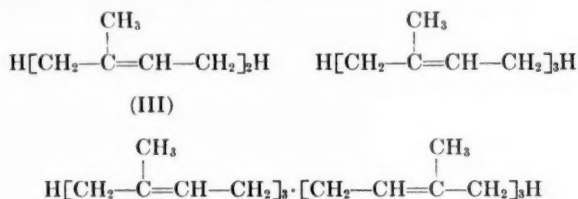
More recently Farmer and Paquot have made new and important contributions to the study of this problem; the work of Farmer deals particularly with rubber. It would appear of value to point out some of the important features of these investigations, so that the importance of this new concept of α -methylene reactivity may be better realized. Moreover, it is possible to apply these same concepts to the phenomena involved in the two modes of protection of rubber against aging which were described some time ago by the present author⁶. With the aid of the more general concept of α -methylenic activity,

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it is possible to define better the hypothesis of aging advanced by the present author by developing it into a more definite concept of the many ways in which oxygen can unite with the rubber molecule, and identifying which of the reactions result in degradation of the rubber molecule.

THE INVESTIGATIONS OF FARMER AND OF PAQUOT

In a series of investigations under the general title of the course of autoxidation reactions of polyisoprenes and allied compounds⁷, Farmer and his collaborators have, by extending the researches of Criegee on cyclohexene⁸, shown that the peroxides formed in the autoxidation of 1-methylcyclohexene and 1,2-dimethylcyclohexene are hydroperoxides of the constitution (I). The same is true of dihydromyrcene (III), farnasene (IV) and squalene (V), all of which may be regarded as polyisoprene hydrocarbons.



These investigators later studied the changes in the unsaturation, hydroxylic oxygen content, and peroxidic oxygen content when rubber undergoes autoxidation. From their experiments, they concluded that, in the first stage of the reaction, oxygen is fixed almost solely on the α -methylenic carbon atoms, with formation of hydroperoxide groups, and not by addition to the double bonds. According to these investigators, it is only subsequently, in secondary reactions, that oxidative scission takes place, with consequent degradation of the rubber molecule. The mechanism of this peroxidation has been discussed in detail in another paper⁸.

On the other hand, Paquot, in a thesis⁹, entitled, "The autoxidation and oxidation of ethylene and benzene hydrocarbons by oxygen catalyzed by phthalocyanines", investigated and identified derivatives obtained from numerous hydrocarbons, and came to the conclusion that the two types of peroxides, I and II, are formed simultaneously in the autoxidation reaction. He assigned to them the structures I' and II', which are slightly different from I and II, and give evidence of the active oxygen which is available.



Paquot designated P_1 peroxide type of oxidation as that which takes place by the intermediary action of a peroxide of the I' type, and P_2 peroxide type of oxidation as that which involves the initial formation of a peroxide of the II' type. In addition to this, in the series of oxidation reactions which take place, it is possible that certain derivatives formed from the peroxide P_1 yield, in turn, peroxides of the P_2 type. This is what Paquot designated by the term P_1P_2 oxidation.

The numerous experiments of Paquot led him to the conclusion that the products characteristic of autoxidation of ethylene hydrocarbons can be explained by two types of oxidation corresponding to the transitory formation of the two peroxides, P_1 and P_2 . Paquot adds the important observation that, with aliphatic hydrocarbons, these two types of oxidation occur in almost equivalent proportions. On the contrary, with cyclic compounds, the P_1 type of peroxide is formed in greater proportion than the P_2 type. This is evidence of the danger that there would be in any attempt to apply the results obtained with a compound in one series of hydrocarbons to the behavior of a compound belonging to another series. This is particularly true of rubber, the behavior of which must not be judged without a great deal of circumspection by the behavior of cyclohexene and its derivatives.

On the other hand, account must be taken of the fact that the experimental procedure chosen by Farmer and his collaborators involves oxidation in an atmosphere of oxygen and in a quartz vessel, without ultraviolet irradiation. Hock chose a similar technique for preparing peroxides in higher yields than by ordinary methods. However, as noted by Paquot, it is reasonable to ask whether, in these experiments, ozone as well as oxygen takes part in the reactions and whether the peroxide may not be formed by partial reduction of an ozonide in addition to the direct fixation of oxygen on the hydrocarbon. On the contrary, in catalysis by phthalocyanines, the reactions are the same as in the case of autoxidation which is not catalyzed, at least from the overall point of view, and as far as the nature of the oxidation products are concerned¹⁰.

Among the compounds studied by Paquot, two compounds, 2-methyl-2-pentene, $(H_3C)_2C:CHC_2H_5$, and particularly 3-methyl-2-pentene, $H_3CCH:C(CH_3)C_2H_5$, should, because their structures approach the linked structure of the molecular chain of rubber, be given special attention. Analysis of the autoxidation products of these two compounds showed for the first compound 54 per cent of the P_1 peroxide and 38 per cent of the P_2 peroxide, and for the second compound 48 per cent of the P_1 peroxide and 27 per cent of the P_2 peroxide. The formation of the P_1P_2 peroxide was 4 per cent for the first compound and 15 per cent for the other compound.

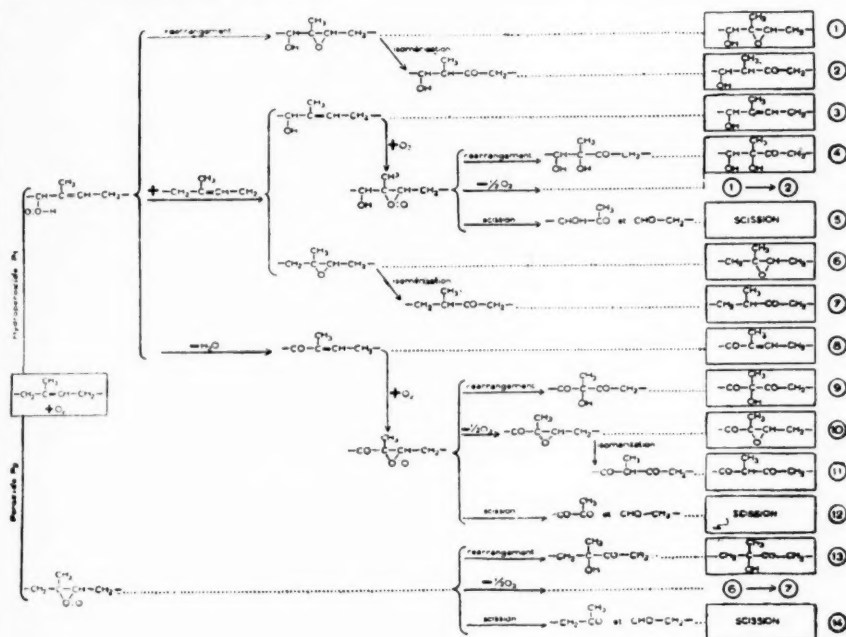
THE AUTOXIDATION OF RUBBER

Based on the experimental results which have just been described briefly, it might be assumed that when rubber undergoes oxidation, P_1 and P_2 peroxides are formed simultaneously. These peroxides form progressively, and are in turn instrumental in the formation of oxidation products.

It seemed to the present author to be of value to clarify these various ideas by showing schematically, and by analogy with the type of compounds identified by Paquot, the principal reactions which are capable of taking place. On this basis, the accompanying tabular arrangement of the reactions has been drawn up. It should obviously not be regarded as a rigidly conceived scheme which represents in any strictly mathematical way the course of autoxidation, but rather a simple guide, showing the possible transformations which each isoprene unit in the molecule may undergo.

It will be seen that the P_1 hydroperoxide may lead: by rearrangement to an epoxy derivative (1) and by isomerization of the latter to a ketone-alcohol (2); by liberation of oxygen or reaction with an isoprene unit to an α -ethylenic alcohol (3) or to an epoxy derivative (6), which can isomerize to a ketone (7); and by dehydration to an α -ethylenic ketone (8).

The cyclic peroxide P_2 may, in turn, form, by reactions analogous to the first two modes of formation of P_1 , either a ketone-alcohol (13) or an epoxy compound (6). On the other hand, it is capable of bringing about cleavage of the molecule at the location of the double bond, with formation of a ketone and of an aldehyde (14).



Finally the alcohol (3) and the α -ethylenic ketone (8) formed by the oxidation according to type P_1 can in turn undergo autoxidation, in which case the peroxides are necessarily of the P_2 type. These peroxides then react, either with formation of ketone-alcohols or epoxy compounds or with resulting cleavage.

It might also be assumed, for example, that an α, α' -ethyleneglycol, $-\text{HC}(\text{OH})\text{C}(\text{CH}_2\text{OH})\text{:CHCH}_2-$, is formed, since the existence of analogous compounds were identified under different conditions by Paquot, or that glycols resulting from the hydration of epoxy derivatives are formed.

However, it is not the intention to discuss in detail at this time all the possible effects of oxygen, nor the probability of these effects. Such as it is, the table suffices to give, in materialized form to some extent, the schemes by which the effects of a typical antioxygenic substance and a deactivator have already been represented¹¹. It is evident that oxygen can combine in various ways with a molecule of rubber hydrocarbon, without bringing about scission, but with formation of various derivatives which may be designated in a general way as oxides of rubber. Unquestionably the entrance of oxygen into the rubber molecule must bring about changes in the physical properties which are manifest in changes in tensile strength and elasticity, but these effects cannot be comparable to the profound degradation resulting from scission. Furthermore one should not fail to take into account the intermolecular reactions which

may take place at the same time, by formation of oxygen bridges and especially as a result of the effect of peroxides acting as polymerization catalysts. These reactions lead to an increase in the three-dimensional cross-linking, and therefore are probably the chief cause of hardening. It is easy to realize the complicated nature of aging by considering the great number of isoprene units in the rubber molecule, for these units may undergo, according to the laws of chance, any one of the changes which have been mentioned.

PROTECTION AGAINST OXYGEN

The problem then arises as to how protective agents enter into the reactions. It should first of all be recalled in what respect the two protective mechanisms can be distinguished. One mechanism involves the antioxygenic effect, properly speaking, and is manifest by a considerable reduction in the rate of absorption of oxygen; the other mechanism has, on the contrary, hardly any influence on this rate of oxygen absorption and, instead, acts by decreasing the deleterious action of the oxygen which has been absorbed. According to the hypothesis advanced by the present author, which depends directly on the doctrine of autoxidation of Dufrasse¹², protective agents belonging to the second category should be essentially deactivating agents. An examination of the table in the present paper might lead one to assume that a typical antioxygenic agent opposes directly the fixation of oxygen on the rubber molecule in the first stage of oxidation and on derivatives (3) and (8) in the secondary stages.

As for the deactivating agent, its role is to direct the oxidation toward reactions in which the oxygen becomes fixed, without resulting scission, on the rubber molecule. Two hypotheses may be offered, either that the deactivating agent prevents the formation of peroxides of the P_2 type, in which case a certain proportion of α -ethylenic ketone and α -ethylenic alcohol would necessarily be found in the autoxidation products; or that the deactivating agent merely acts as a barrier to the scission reactions, and in every case diverts the evolution of peroxides toward other types of transformations. The term deactivating agent as previously suggested is not, therefore, perhaps very suitably chosen, and since it is not, strictly speaking, a question of a deactivating effect, it might be preferable to speak of a diverting action and of a diverting agent. If future experiments ultimately prove that it is the formation of P_2 peroxides which such an agent really opposes, then it would be logical to qualify the agent either as an α -diverting agent or as a hydrodiverting agent, according to whether particular stress is laid on the preferential reactivity of the α -methylene carbon atom or on the nature of the hydroperoxide.

In practice, as has been proved by the present author in comparative tests of various protective agents, in which the oxidizability and the deterioration of physical properties by artificial aging were measured, each protective substance appears to involve a complex of two mechanisms, whereby in each case one or the other of these mechanisms is more or less predominant. The percentage of oxygen which is harmful and which causes deterioration in mechanical properties is, then, characteristic of each individual protective agent, and its value, in relation to the value for the corresponding unprotected control sample, gives an indication of the antioxygenic or diverting character of the mechanism concerned.

It is easy to see that the optimum protection is obtained by the judicious choice of two agents, one of which has the greatest possible antioxygenic power,

so as to oppose to a maximum degree combination of oxygen with rubber; the other, the greatest possible diverting power so as to orient toward the formation of the least harmful derivatives the oxygen which escapes the barrier set up by the first agent. This theoretical consequence of the hypothesis has, in fact, been confirmed by actual experiment¹³.

Finally, to prove that these mechanisms are operative and to explain fully their nature, it would be of particular interest to continue the studies of autoxidation which have been described, operating this time in the presence of a typical antioxygenic substance and also in the presence of a diverting agent. A first step might be to study the methylpentenes already examined by Paquot, and by comparing the respective proportions of the P_1 and P_2 peroxides, to have a means of determining to what extent the two types of protective agents play a part in orienting the reactions. After this, the investigation might take up the peroxidation of rubber, as was done by Farmer and Sundralingam¹⁴. It might be expected that there would then be available experimental facts of sufficiently precise a nature to make it possible to explain completely the complicated mechanism of protection against the deteriorating action of oxygen. However, it must be realized that these studies might prove to be unfruitful because of the complexity of the compounds formed in the oxidation of so large a molecule and because of the difficulties which may be foreseen in separating and identifying them.

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POLYPRENE AND THIOGLYCOLIC ACID *

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By the prolonged action of thioglycolic acid on small strips of crude Hevea rubber, the present author many years ago¹ obtained a product of the composition, $C_5H_{8.90}O_{0.01}(SCH_2CO_2H)_{0.95}$, which was soluble in alkalies, and a similar product from balata, whereas under the same conditions gutta-percha did not react to any significant extent with thioglycolic acid.

In benzene solution the addition of thioglycolic acid to rubber proceeds very slowly. It was found that a combination of the two methods, whereby the two reagents were dissolved in benzene, the benzene then allowed to evaporate spontaneously and the residue allowed to stand in the open air for some time, offered an easy means of carrying the reaction to completion, although the rubber was partially oxidized at the same time.

In the procedure described in the present paper, the new method was employed as recently applied to the determination of the rubber contents of samples which were prepared in Svalöv in connection with development work on the rubber-bearing dandelion, *Taraxacum kok-saghyz* Rodin², carried out by the Sveriges Utsädesförening. As a means of comparison, the experiments were repeated in the same way with crude Hevea rubber, which had been obtained nine years before from the Hälsingborg Gummifabrik A.-B., and had been treated similarly at that time.

Of the samples of kok-saghyz³, those designated by the symbols Sv 1, Sv 2a and Sv 2b came from plants grown in Svalöv; those designated by the symbol Ham. came from experimental cultivations in Hammenhög. With the exception of sample Sv 2b, the samples of kok-saghyz consisted of large, slightly sticky masses of agglomerated small balls of a brown-gray color, previously used in analytical determinations of the rubber content of the roots of different plants. Sample Sv 2b was obtained in the same way, but since it was very sticky and was dark brown, it was necessary to give it special treatment. An elementary analysis of sample Sv 1 showed 0.38 per cent moisture and 4.56 per cent ash, and, calculated on the dry, ash-free product, 84.51 per cent carbon and 11.39 per cent hydrogen, corresponding to the empirical composition: $C_5H_{8.03}O_{0.18}$. In contrast to this, the Hevea rubber, designated Hev. in Tables 1, 2 and 3, was free of moisture and yielded no ash; it contained 86.77 per cent carbon and 11.65 per cent hydrogen, corresponding to the composition: $C_5H_{8.00}O_{0.07}$.

Treatment with thioglycolic acid was carried out in the following way. First a sample of the rubber was cut into narrow strips, and 5 grams was digested in 100 cc. of benzene. This gave a gelatinous mass, which on the next day was agitated with 10 grams of thioglycolic acid. With Hevea rubber, the mixture soon became thinly liquid, whereas with the samples of kok-saghyz

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the mixtures remained viscous and gelatinous even after 24 hours. After having stood for 24 hours in a closed vessel, the benzene was allowed to evaporate spontaneously, and after one week, during which the residue was kneaded thoroughly, the product was treated with a solution of 5 grams of sodium hydroxide in 100 cc. of water. Under these conditions Hevea rubber yielded an opalescent solution, which, treated with 30 cc. of 5-normal hydrochloric acid, gave an emulsion from which a curdy precipitate rapidly separated. This precipitate, which by the following day had agglomerated to a rubberlike mass, was digested six times in 100 cc. of warm water; the last water was practically free of acid. The product, which was semifluid when warm and an elastic-plastic mass when cooled, was dried over phosphorus pentoxide in a vacuum; this gave a friable, pulverizable mass. After the cream colored powder was dried further in the same way, it was weighed, and an elementary analysis was made⁴.

With the samples of kok-saghyz, the alkali solution left residual undissolved gelatinous masses, which, after being washed with water and dried on clay plates, remained in the form of cutaneous flakes. As obtained from sample Sv 1, these yielded 22.60 per cent of ash. From the solutions obtained by filtration of these masses, the reaction products were isolated in the same way as was the product from Hevea rubber, and they had about the same appearance and properties as the product from Hevea rubber.

The yields and the elementary analyses of the various products are shown in Table 1.

TABLE 1

Sample	Undissolved (g.)	grams	Rubber-thioglycolic acid product			
			C	H	O	S
Sv 1	0.5	7.0	55.96	7.71	19.62	16.71
Sv 2a	0.6	7.3	56.61	7.82	19.12	16.45
Sv 2b	0.5	7.0	55.70	7.77	19.32	17.21
Ham.	0.5	7.6	56.00	7.64	19.58	16.78
Hevea	—	9.5	56.54	7.88	18.92	16.66

From the percentage compositions given in Table 1, it was possible to derive empirical formulas, as shown in Table 2, for the rubber-thioglycolic acid products and for the components containing no thioglycolic acid.

TABLE 2

Sample	Rubber-thioglycolic acid product	Rubber component
Sv 1	$C_5H_{8.42}O_{0.25}(SCH_2COOH)_{0.72}$	$C_5H_{7.70}O_{0.25}$
Sv 2a	$C_5H_{8.45}O_{0.23}(SCH_2COOH)_{0.70}$	$C_5H_{7.73}O_{0.23}$
Sv 2b	$C_5H_{8.55}O_{0.19}(SCH_2COOH)_{0.75}$	$C_5H_{7.80}O_{0.19}$
Ham.	$C_5H_{8.52}O_{0.24}(SCH_2COOH)_{0.72}$	$C_5H_{7.59}O_{0.24}$
Hevea	$C_5H_{8.52}O_{0.19}(SCH_2COOH)_{0.71}$	$C_5H_{7.81}O_{0.19}$

The agreement in composition of the various products is accordingly good. The oxidizing effect of atmospheric oxygen on the rubber indicates that in each case approximately 25 per cent of the double bonds of the rubber have reacted with oxygen, and that a certain amount of hydrogen has disappeared at the same time. The yields with respect to the rubber components of the compositions shown in Table 2 and their conversion to yields based on pure rubber, C_5H_8 , are shown in Table 3.

Since Hevea rubber gave a yield of 95 per cent based on pure rubber, the pure rubber content of the kok-saghyz samples might be expected to be around

TABLE 3

Sample	Rubber components		Pure rubber, C ₅ H ₈	
	Percentage based on sample	Percentage based on dissolved part	Percentage based on sample	Percentage based on dissolved part
Sv 1	73	81	69	77
Sv 2a	77	87	73	83
Sv 2b	71	79	68	76
Ham.	79	88	75	83
Hevea	99	99	95	95

75 to 80 per cent. The remaining 25 to 20 per cent comprises benzene-insoluble salts of high-molecular organic acids, as well as other substances, *e.g.*, inulin, which are lost during the experimental operations.

The sample of Hevea rubber used in the present work had been newly acquired from the manufacturer⁵, had been treated with thioglycolic acid as described above, and the residue from the evaporation protected from the air for one month; 5 grams of sample yielded 9.6 grams of rubber-thioglycolic acid, which contained 53.48 per cent carbon, 7.32 per cent hydrogen, 21.53 per cent oxygen, and 17.67 per cent sulfur, corresponding to the composition, C₅H_{8.37}O_{0.36}(SCH₂CO₂H)_{0.82}, with the rubber component of the empirical composition, C₅H_{7.55}O_{0.36}. Hence in this case oxidation had proceeded still further than when the corresponding residue from the evaporation had been analyzed after only one week.

A sample of balata which was prepared by coagulation of balata latex with acetone⁶ and was washed in the form of thin strips with water and acetone, yielded, on treatment of 4 grams with thioglycolic acid⁷ by the same method used for Hevea rubber as just described, 7.8 grams of balata-thioglycolic acid product, containing 52.03 per cent carbon, 7.50 per cent hydrogen, 21.42 per cent oxygen, and 19.05 per cent sulfur, corresponding to the empirical composition: C₅H_{9.00}O_{0.24}(SCH₂CO₂H)_{0.95}, with the thioglycolic acid-free component, C₅H_{8.05}O_{0.24}. A sample of gutta-percha, prepared from gutta-percha latex by the same method, yielded, by treatment of 4 grams in the same way with thioglycolic acid, 5.5 grams of gutta-percha-thioglycolic acid product, containing 51.60 per cent carbon, 7.58 per cent hydrogen, 22.06 per cent oxygen, and 18.76 per cent sulfur, corresponding to the empirical composition: C₅H_{9.22}O_{0.33}(SCH₂CO₂H)_{0.94}, with a thioglycolic acid-free component of the composition: C₅H_{8.25}O_{0.33}. These results show that when the three polyrenes, rubber, balata and gutta-percha, are treated with thioglycolic acid by the method described, they all behave in the same general way.

A sample of kok-saghyz rubber (Ham.) was treated also with thiohydroacrylic acid. Five grams of sample in 100 cc. of benzene, treated with 11 grams of thiohydroacrylic acid in exactly the same way as with thioglycolic acid, yielded 0.3 gram of insoluble gel and 10 grams of alkali-soluble product. The latter contained 56.41 per cent carbon, 8.05 per cent hydrogen, 18.72 per cent oxygen, and 16.82 per cent sulfur, corresponding to the empirical composition: C₅H_{8.59}O_{0.19}(SCH₂CH₂CO₂H)_{0.84}, with a rubber component of the empirical composition: C₅H_{7.75}O_{0.19}. At the same time, a significant yield of dithiodihydroacrylic acid was obtained, whereas in a similar experiment with Hevea rubber, no dithiodihydroacrylic acid was formed, nor did the rubber react to any noteworthy extent.

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- ⁴ The author is indebted to (Miss) Majbritt Lindström for making this analysis.
- ⁵ This experimentation was carried out in connection with the work of civil engineer O. Samuelson at the Technical Institute in 1937-1938.
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CARBON AND HYDROGEN IN RUBBER HYDROCARBON *

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Analyses by combustion of rubber hydrocarbon separated from rubber latex and crystallized from ethereal solutions at low temperatures¹ yielded combined percentages of carbon and hydrogen which totaled slightly less than 100. Midgley, Henne, Shepard and Renoll² assumed the difference to be due to oxygen, and they have used the results to substantiate their argument that natural rubber is not a true hydrocarbon but contains a small amount of oxygen in chemical combination.

Later, Roberts³ reported that he had isolated the portion of rubber which contained oxygen. This he called caoutchol to distinguish it from the hydrocarbon, which he named caoutchene. He used Midgley's results to confirm his findings, which he attempted to apply in a new way to the familiar two-phase theory of Fessenden as an explanation of the properties of rubber. However, Schidrowitz⁴ has indicated that the method used by Roberts to separate the caoutchol is not free from possible criticism. Some steps in the procedure, *e.g.*, milling, promote oxidation.

Since publication of the analyses made at the Bureau of Standards, the values for the atomic weights of carbon and hydrogen have been changed from 12.00 and 1.0078 to 12.010 and 1.0080, respectively. When these earlier results are recalculated with the new atomic weights, the sums of carbon and hydrogen are increased by 0.061 per cent. When the results reported in the earlier paper are corrected for two typographical errors and this increment is added, the recalculations are as shown in Table 1.

Several things should be said about these results if they are to be used as a basis for judging whether oxygen constitutes a part of the normal rubber molecule. (1) The sum of carbon and hydrogen found increased with increasing purification of the rubber. (2) The most carefully purified material gave an average sum of carbon and hydrogen in excess of 100 per cent, and the four analyses of hydrocarbon which had been recrystallized at least once averaged 99.97. (3) The differences between analyses of the same material were greater than the average difference between the sum of hydrogen and carbon and 100 per cent. The latter cannot, therefore, be regarded as certainly significant. (4) The absolute purification of the rubber hydrocarbon cannot be assumed. Substantially all probable impurities, including water, ether, dissolved or adsorbed gases, inorganic material, and products of oxidation of the rubber itself, would have lowered the sums of hydrogen and carbon observed.

Certainly the results leave very little, if any, of the weight of the rubber to be accounted for as normally combined oxygen. This is not all, however. The observed ratio of hydrogen to carbon is higher than the theoretical (0.1343) by an amount that appears less significant than it really is, in comparison with

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TABLE I
COMPOSITION OF RUBBER (RECALCULATED)

	Hydrogen	Carbon	Sum	Ratio hydrogen: carbon
Rubber hydrocarbon uncrystallized	11.85	88.03	99.88	0.1346
	11.84	88.11	99.95	0.1343
	11.77	87.66	99.43	0.1342
	11.85	88.03	99.88	0.1346
	11.82	87.92	99.74	0.1344
Average			99.78	
Crystallized once	11.86	88.06	99.92	0.1346
	11.82	88.02	99.84	0.1343
Average			99.89	
Crystallized three times	11.87	88.31	100.18	0.1344
	11.86	88.13	99.99	0.1345
Average			100.05	
General average			99.87	

the total weight of carbon and hydrogen, because of the small weight of hydrogen. For the entire series of analyses the weight of carbon dioxide found was 0.21 per cent lower than that computed from the weight of rubber burned, the weight of the water being only 0.06 per cent low. For the four samples of recrystallized rubber, the carbon dioxide was 0.09 per cent low and the water 0.08 per cent high. These differences are in the direction we would expect if the discrepancy in the total weight were the result of probable impurities in the rubber, particularly water and ether; on the other hand, the presence of oxygen combined as hydroxyl would not affect the ratio of hydrogen to carbon, and in the form of other probable radicals it would reduce that ratio.

If the small difference between the theoretical value and the sum of hydrogen and carbon is to be considered significant, the difference between their theoretical and observed ratios must also be significant, and this definitely indicates incomplete purification rather than combined oxygen, as postulated by Midgley.

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MOLECULAR WEIGHT OF GR-S FRACTIONS

SIMPLE GLASS OSMOMETER FOR USE IN HYDROCARBON SOLVENTS *

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Measurements of molecular weights of high polymers by the osmotic pressure method are most commonly made with metal osmometers such as those described by Fuoss and Mead¹, Flory², and others³. These instruments are expensive and somewhat difficult to construct and operate. This report describes a small, inexpensive, all-glass osmometer⁴ which may be made and used in large numbers; it is somewhat different from simple glass osmometers described elsewhere⁵. The instrument, shown in Figure 1, consists of a capillary

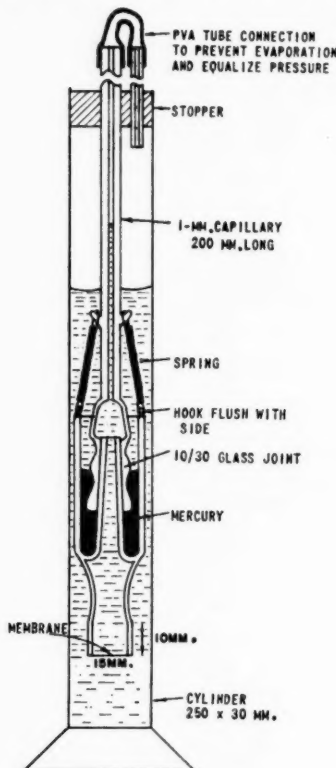


FIG. 1.—Osmometer.

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tube connected to a mercury-sealed ground-glass joint, on the lower end of which is a short tube 15 mm. in diameter. The joint is held together with steel springs, and the bottom of the osmometer is fastened to a membrane by means of a polyvinyl alcohol cement as described below.

The osmometer has certain advantages. Its volume is only about 5 cc.; it is inexpensive and easily constructed; it may be quickly and easily filled; and it seldom develops leaks. On the other hand the membrane area is small, necessitating a wait of several days for equilibrium to be established, and because of the method used for fastening on the membrane it is recommended only for hydrocarbon solvents.

Using this osmometer, osmotic pressures were measured on a sample⁶ of GR-S and on eight fractions of this material. The results of the fractionations and viscosity measurements⁷ are shown in Table I and Figure 2, where the

TABLE I
RESULTS FROM OSMOTIC PRESSURE MEASUREMENTS OF
GR-S SOLUTIONS IN BENZENE AT 30° C

Designation	$(h/C_u)_0$	Molecular weight (number average)	$[\eta]$	b	μ_1
Unfractionated polymer	280	92,000	2.37	1.7×10^{-3}	0.36
Fraction 4P1	28	920,000	4.74	1.5	0.38
Fraction 4P2	55	470,000	3.28	1.6	0.37
Fraction 4P3	80	320,000	2.37	.	.
Fraction 4P4	105	220,000	1.92	1.6	0.37
Fraction 4P5	200	130,000	1.22	1.7	0.36
Fraction 4P6	600	43,000	0.68	1.9	0.35
Fraction 4P7	1010	25,400	0.42	5.1	0.09
Fraction 4P8	(2580)?	(10,000)	0.30	(5.6)?	(0.05)?

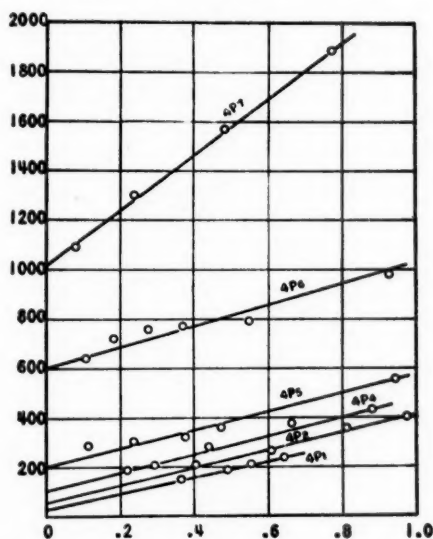


Fig. 2.—Variation of reduced osmotic pressure with concentration, GR-S in benzene at 30° C.

reduced osmotic pressure is plotted against concentration. The slope of the curves, b , as recorded in Table I is observed to decrease with increasing molecular weight. This is believed to be due to increasing branching of the polymer chain as the molecules grow larger during polymerization, and is observed in other systems⁸.

The units used in Table I are explained below in the section on calculation. $(h/C_w)_0$ is the value of the ordinate in Figure 2 at zero concentration. The values of b are proportional to the slopes of the curves (cf. Figure 2), from which they are obtained by means of Equation 5.

The molecular weight values in Table I for GR-S fractions and other values found later correlate with intrinsic viscosity in toluene at 30° C in a manner shown in the following equation:

$$[\eta] = 5.4 \times 10^{-4} M^{0.66}$$

where M is the number average molecular weight of the fractions and $[\eta]$ is the intrinsic viscosity as determined with the concentration of solute in grams per 100 cc. of solution.

This relationship has been confirmed by R. H. Ewart, H. C. Tingey, and M. Wales of these laboratories, who obtained $[\eta] = 4.9 \times 10^{-4} M^{0.67}$, and also by Scott and Magat⁹, who obtained $[\eta] = 5.5 \times 10^{-4} M^{0.67}$. The form of this expression is not unexpected in view of much previous work¹⁰.

EXPERIMENTAL

Membranes.—Perhaps the most important and difficult factor in the measurement of osmotic pressure is the nature and use of the membrane. Membranes used with high molecular substances should have the following characteristics:

Their permeability should be such that impurities of low molecular weight diffuse easily through them, yet no part of the solute being measured should pass.

The membrane should be inert and insoluble in the solvent being used.

The membrane should not be extensible and should not change its shape, wrinkle, or buckle during the measurements.

In practice four types of membranes have been most satisfactory for non-aqueous solvents: cellophane regenerated but undried³, cellophane swollen with sodium hydroxide or zinc chloride solutions¹¹, collodion reduced by denaturation to cellulose¹², and Zsigmondy Ultracella "fine" and "finest". The latter is made of cellulose and gelatin¹³.

In these experiments nonwaterproofed cellophane 1 mil thick swollen with 57 to 64 per cent solutions of zinc chloride was used. After swelling, the membranes were washed in a mixture of 0.5 volume triethyleneglycol and 0.5 volume of water. The membranes could then be placed in air without becoming dry and impermeable.

The membranes were graded according to thickness as follows:

Grade	Thickness (mils)	Average "permeability constant" for benzene $P \times 10^5$
1	2.5-3	16
2	3-4	29
3	4-5.5	65

$$\text{where } P = \frac{a \ln S_0/S_t}{At}$$

a is the cross-sectional area of the glass capillary

A is the area of the membrane

t is the time in hours

S_0/S_t are the positions of the meniscus of benzene at time zero and time t

These values of the "permeability constant" compare with 100 to 300 for some reduced collodion films and with 70 to 250 for Zsigmondy Ultracella fine. Drying the membranes reduces their permeability to about a tenth of the above. Depending on the grade of membranes used, polymers of from 10,000 to 100,000 average molecular weight show erratic osmotic pressures because of diffusion of low molecular weight material through the membrane. In general, grade 3 films were too permeable for any except the highest molecular weight, while films less than 2.5 mils thick were used on one occasion down to 10,000 molecular weight.

Sodium hydroxide is now preferred as a swelling agent, since regulation of concentration is less critical than with zinc chloride. The present method of membrane preparation is to staple No. 300 Sylvania Corp. cellophane to a wire frame and soak overnight in a 40 per cent sodium hydroxide solution. The membranes are then washed for 2 hours under running water and finally soaked for 3 hours in 50 per cent by volume triethyleneglycol solution. They are then smoothed out on a glass plate, covered with filter paper, and allowed to stand overnight. This swelling procedure increases the thickness from 0.0008 to about 0.003 inch (0.002 to 0.0075 cm.).

Sealing on the membranes.—The membranes are sealed to the open bottom of the osmometers with a polyvinyl alcohol cement made from 30 grams of polyvinyl alcohol¹⁴ and 100 cc. of cold water, heated and strained. Polyvinyl alcohol is allowed to come in contact with both the inside and outside of the end of the tube. A piece of the membrane moist with triethyleneglycol is laid flat on a piece of paper and the wet tube pressed on it. The tube is then inverted and held in place for about an hour. More polyvinyl alcohol is then put around the joint with the end of a length of wire and the osmometer is clamped right-side up and the cement is allowed to dry for at least 16 hours and finally baked 15 minutes at 100° C just before filling. Failure to bake the membranes and cement may cause them to shrink and change shape during the measurements.

Water will be removed during the baking, but the triethyleneglycol remains and enables the membranes to stay permeable. The triethyleneglycol is subsequently washed out in the solvent. Membranes sealed on in this way may be used several times in succession, provided they are not allowed to become dry.

Because of the nature of the cement, polar solvents are not recommended. However, some measurements have been made in methylethyl ketone. No osmotic effects have ever been observed with Solvar 5/7 polyvinyl alcohol in benzene.

Filling the osmometers.—About 35 cc. of a 1 per cent solution of the polymer whose molecular weight is to be measured are made up and diluted so as to obtain four or five 10-cc. solutions at various concentrations between 0 and 1 per cent. The solution is poured into the osmometer bottom and allowed to overflow into the cup of the mercury seal. By means of a rubber tube connected to the top of the capillary, solution from the cup of the mercury seal is sucked up through the partially opened ground-glass point to the desired place and the osmometer halves are connected. After the cup is rinsed, mercury is poured into the mercury seal and the osmometer is inserted in a glass cylinder containing solvent.

The cylinder is placed in a 30° C constant-temperature bath and allowed to come to temperature equilibrium. The level of the meniscus in the capillary is then adjusted to whatever position is required. Pressure readings are made by a cathetometer and are corrected for the capillary rise of the solution in each osmometer.

Calculations.—The relationship between the osmotic pressure, π (dynes per sq. cm.²), and the concentration, C (grams per cc.), may be conveniently expressed without any significant inaccuracy by the relation:

$$\frac{1}{RT} \times \frac{\pi}{C} = \frac{1}{M} + bC \quad (1)$$

provided the polymer concentration is, in general, of the order of 0.010 gram per cm.³ or less. Huggins¹⁵ in a more general treatment gives constant b the value:

$$b = \frac{1}{V_1 d_1^2} \left(\frac{1}{2} - \mu_1 \right) \quad (2)$$

(V_1 is molal volume of solvent; d_1 and d_2 are densities of solvent and polymer, respectively; g is acceleration of gravity; and R , the gas constant, is 8.31×10^7 dyne cm. per mole degree.) The calculated values of Huggins' constant, μ_1 , are given in Table I.

The measured quantities are the osmotic height, h (cm.), and the weight concentration, C_w (grams of solute per gram of solvent). In terms of these:

$$\frac{C_w}{h} = \frac{RT}{g} \times \frac{1}{M} + b'C_w \quad (3)$$

Values of the reduced osmotic height, (h/C_w), are plotted against the weight concentration and the plot is extrapolated linearly to zero concentration to obtain (h/C_w)₀ and the slope, b' .

The number average molecular weight of the polymer, M , and the constant, b , are then calculated from:

$$M = \frac{RT/g}{(h/C_w)_0} = \frac{8.477 \times 10^4 T}{(h/C_w)_0} \quad (4)$$

$$b = \frac{b'}{d_1(RT/g)} \quad (5)$$

Reproducibility of results.—For one fraction of GR-S the osmotic pressure was taken three times with different membranes of the same permeability, the solutions being made up each time from the stock solution. Values of 31.0, 30.8, and 31.4 mm. were obtained.

For a sample of whole GR-S, measurements were made with membranes of different permeability.

Concentration (%)	% Solution of ZnCl ₂ used on membranes	Osmotic pressure (mm. of solution)
0.927	55	55
	57	59
	60	57
	63	56
	55	13.9
0.309	57	12
	60	12.3
	63	12.3

SUMMARY

Osmotic molecular weight measurements have been made on a sample of unfractionated GR-S and on eight fractions of this material. The molecular weights ranged from 10,000 to approximately 1,000,000, with a number average at 92,000. The relationship between molecular weight and viscosity for GR-S was determined. A simple all-glass osmometer for use in hydrocarbon solvents is described, and information on its use and the membranes employed is given.

ACKNOWLEDGMENT

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SOLUBILITIES OF UNVULCANIZED RUBBERS *

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Solubility studies on unvulcanized rubbers are very useful both to indicate types of materials most likely to be good solvents and softeners and to indicate the effect of various solvents and oils on vulcanized rubbers. Furthermore, such studies are so simple and relatively economical of time and effort that they make possible the accumulation of a broad background of data which would be impractical to obtain by other means.

By investigating the effect of a wide variety of solvents on a single rubber it is possible to tell which groups have good solvent action and which do not. This information makes it possible to predict, with considerable accuracy, the solvent power of any material of known composition. The solvent power of a given material, together with chemical stability, boiling point, melting point, and viscosity, indicates quite well its utility as a softener. In many cases the nature of the solution also indicates whether or not the material is an effective tackifier. The usefulness of such solubility data in cement manufacture is obvious.

It is generally true that materials which are good solvents for an unvulcanized rubber are strong swelling agents for the same rubber when vulcanized. Here also such properties as melting point and viscosity have an important bearing on the time required to reach equilibrium and on the permanence of the swelling action.

In agreement with the above views, solubility studies were carried out during the early evaluation of a number of synthetic rubbers. Solvents were selected so as to show the effect of various functional groups, different types of hydrocarbon radicals, chain length and branching in aliphatic radicals, and molecular weights. Allowances were made for differences in viscosity and molecular weight. These studies were then used both for the selection of cement solvents and softeners and for predicting the utility of the rubbers for various types of solvent resistance. These studies proved so useful that they have recently been brought up to date for publication.

PROCEDURE

The elastomers were masticated on a warm mill until broken down. The 1/32-inch rubber sheets were then rolled into parchment directly off the mill. The plasticized polyvinyl chloride (Koroseal sheet, 59 per cent polyvinyl chloride, 41 per cent tricresyl phosphate) used in this study was compounded, milled, and molded into 1/32-inch sheets. Approximately 20 cc. of the solvents was placed in small vials, and 0.5 gram of the freshly prepared elastomer was added. All vials were kept at room temperature except those containing phenol, tertiary butylcatechol, and ethylpentachlorobenzene. These were

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kept at temperatures above their melting points. Observations were made after two and four hours and one, five, and seven days. The vials were thoroughly stirred before each inspection.

DESCRIPTION OF RESULTS

For maximum convenience the results have been condensed into a coded table. The table takes into account two factors, rate of change and type of change. Where the observed change was essentially complete within one day, the rate was fast—F. If the change was incomplete in one day, but apparently complete in 5–7 days, the rate was moderate—M. If an apparently continuous change was incomplete at the end of seven days, the rate was slow—S. The types of change are classified as (1) dissolved—D, (2) limited swelling and(or) softening—L, and (3) unlimited swelling, or gelatinized—G. Where there was no apparent action the simple designation—N—for no change is used.

The following examples illustrate the significance of the terms:

Hycar OR-15 is essentially unaffected by hexane, as indicated by N. Obviously this means only that within the limits of precision of the test no change was observed. There may have been either small swelling or small shrinkage. It is obvious, however, that aliphatic hydrocarbons would be poor softeners. It is also very probable from these tests that vulcanized Hycar OR-15 has good resistance to aliphatic hydrocarbon solvents. This fact is adequately demonstrated by other published data on Hycar OR-15 and by actual service testing.

GR-I was completely dissolved in hexane within 24 hours, as indicated by FD. In kerosene it dissolved more slowly and required more than seven days for complete solution. This is shown as SD. In mineral oil there was little change the first day, followed by swelling and gelling. At the end of seven days it was thoroughly gelled and partially dissolved; hence the designation MG. The results indicate that the aliphatic hydrocarbons are good softeners and solvents for GR-I. Vulcanized GR-I swells greatly in aliphatic hydrocarbons, and the rate of swell decreases with increasing molecular weight and viscosity. These predictions are also borne out by actual service tests.

GR-S shows rapid, but limited swelling in nitropropane—FL. In 2-chloroethanol the swelling is limited, but slower as indicated by ML. Since both hexane and 1,2-dichloroethane are good solvents, it is indicated that the nitro group and the hydroxyl tend to decrease softener action and also to decrease the swelling effect of solvents on vulcanized GR-S.

INTERPRETATION OF RESULTS

In using these solubility data in finding the answers to practical questions which frequently arise in rubber practice, it should be realized that the study was made on pure-gum unvulcanized elastomers and that application of the data to vulcanizates necessitates the use of considerable discretion on the part of the interpreter. A solvent which quickly dissolves a pure-gum unvulcanized rubber naturally does not dissolve a compounded vulcanizate, but tests have shown it to be generally true that a solvent which quickly dissolves a gum has a pronounced swelling action on the corresponding vulcanizate. A solvent which only gells or swells the gum shows somewhat less swelling on the vulcanizate and, of course, one which apparently has no effect on the gum has the least swelling effect on the vulcanizate. Similarly, the fact that two differ-

Key	Type of action	Boiling point (°C, 760 mm.)	Natural pale crepe	German Buna-S	GR-S	Hycar OS-10	Butadiene- methylmethacrylate copolymer	GR-I (Butyl)	GR-M (Neoprene)	Perbunan No. 26	Hycar OR-15	GR-P (Thiokol)	Plasticized polyvinyl chloride
R—Rapid	L—Limited swelling and/or softening												
S—Slow	G—Gelling or unlimited swelling												
M—Moderate	D—Dissolving												
F—Fast	N—No apparent effect												
	SOLVENT												
I. HYDROCARBONS													
A. Aliphatic													
	Hexane	69	FD	FD	FD	MG	MD	FD	MD	SL	N	N	N
	Hi-Test gasoline	38-141	FD	FD	FD	FL	FD	FD	ML	SL	N	N	N
	Kerosene	165-257	FD	SD	SD	FL	FD	SD	SL	N	N	N	N
	Mineral oil (amline point 104° C)	—	FG	MG	MG	ML	MG	MG	SL	ML	N	N	N
B. Alicyclic													
	Cyclohexane	80.8	FD	FD	FD	MD	FD	FD	MD	SL	N	N	N
C. Terpene													
	Pinene	156	MD	MD	MD	FG	FD	MD	MD	FL	FL	N	SL
	Dipentene	175-190	FD	FD	FD	MD	FD	FD	FD	FL	N	ML	SL
	Turpentine	160-180	FD	FD	FD	MD	FD	FD	FD	FL	N	ML	SL
D. Aromatic													
	Benzene	80.4	FD	FD	FD	FD	FD	FD	FD	FD	FL	FD	N
	Toluene	111	FD	FD	FD	MD	FD	FD	FD	FD	FL	FL	N
	Xylene	138-142	FD	FD	FD	MD	FD	FD	FD	FD	FL	FL	N
	p-Cymene	175-176	FD	FD	MD	MD	FD	MD	FD	MD	FL	ML	N
	Ethylbenzene	135.7	FD	FD	MD	MD	FD	MD	FD	FD	FL	FL	N
	Styrene	145-146	FD	FD	MD	MD	FD	MD	FD	FD	FL	FL	N
	Tetrahydronaphthalene (tetralin)	205	FD	FD	SD	SD	FD	MD	FD	MD	MG	FD	N
	Amylnaphthalene	279-310	MD	SD	SD	SD	MD	MD	FD	MG	SG	FL	N
II. HALOGENATED HYDROCARBONS													
A. Aliphatic													
	Chloroform	61.2	FD	FD	FD	FD	FD	MD	FD	FD	FD	FD	ML
	Carbontetrachloride	76.7	FD	FD	FD	FD	FD	FD	FD	FL	N	N	N
	1,2-dichloroethane	83.5	FD	FD	FD	FD	FD	FG	FD	FD	FD	FD	SD
	Isopropyl chloride	35	FD	FD	FD	FD	FD	FD	FD	FD	FG	ML	FL
	Dichlorodifluoromethane (Freon No. 12)	-28	FG	SD	SD	SL	SL	SG	N	N	N	N	N
	Dichlorofluoromethane (Freon No. 21)	8.9	FD	SD	SD	MD	SD	MD	FG	FD	MD	MD	FL

Key		Boling point (°C, 760 mm.)	Natural pale crepe	German Buna-S	GR-S	Hycar OS-10	Butadiene- methacrylate copolymer	(GR-I (Butyl))	(GR-M (Neoprene))	Perbunan No. 26	Hycar OR-15	GR-P (Thiokol)	Plasticized polyvinyl chloride
Rate of action	Type of action												
35	—	—	FD	FD	FD	FD	FD	MD	FD	FD	FD	FD	FD
28	—	—	FG	SL	SL	SL	SL	SG	N	N	N	N	N
8.9	—	—	FD	SD	SD	SD	SD	MD	FG	FG	MD	MD	FL
<p> Dichlorodifluoromethane (Freon No. 12) Dichlorodifluoromethane (Freon No. 21) </p>													
<p> Key Rate of action S—Slow M—Moderate F—Fast </p>													
<p> Type of action F—Limited swelling and (or) softening G—Gelling or unlimited swelling D—Dissolving N—No apparent effect </p>													
SOLVENT													
II. HALOGENATED HYDROCARBONS—Continued													
B. Aromatic													
Chlorobenzene													
Fluorobenzene													
Chlorotoluene													
Ethylpentachlorobenzene													
o-Chloronaphthalene													
Halowax oil													
Amylchloronaphthalene													
III. HYDROXY COMPOUNDS													
A. Alcohols													
Ethyl alcohol													
Isopropyl alcohol													
Amyl alcohol													
Benzyl alcohol													
Ethylene glycol													
Diethylene glycol													
Glycerol													
Terpinol													
B. Phenols													
Phenol													
Cresol													
p-Tertiary butylcatechol													
IV. CARBOXY ACIDS													
Glacial acetic acid													
Lactic acid													

KEY	Rate of action	Type of action	Boiling point (°C, 760 mm.)	Natural pale crepe	German Buna-S	GR-S	Hycar OS-10	Butadiene- methylethacrylate copolymer	GR-I (Butyl)	GR-M (Neoprene)	Perbunan No. 26	Hycar OR-15	GR-P (Thiokol)	Plasticized polyvinyl chloride
SOLVENT														
V. ETHERS														
Diethyl ether			34.5	FD	FD	MD	MD	FD	FG	FL	N	N	N	N
Isopropyl ether			68.4	FD	FD	FD	SD	FD	FG	FL	N	N	FL	N
Phenylethyl ether			172	MD	MD	MD	MD	FD	MG	SD	N	N	N	N
Dibenzyl ether			295-298	MD	MD	MD	MD	FD	N	MD	MD	MD	SD	SL
Dioxane			101.1	SD	SD	SD	MD	FD	N	FD	MD	MD	FD	FL
Dioxolane			74	FL	SD	FD	FL	FD	FL	SD	MD	MD	MD	FL
VI. AMINES														
Ethylenediamine			117.2	N	N	FL	ML	N	N	N	N	N	SD	N
Dicyclohexylamine			115-116 (8 mm.)	FG	FG	FL	SD	SD	FG	FG	N	N	ML	N
Diethylamine			55-56	N	N	N	N	N	N	N	FG	N	N	N
Aniline			184.4	N	N	SL	MG	FL	N	FL	MD	MD	MD	N
Dimethylaniline			194	FD	FD	FD	FD	FD	MG	FD	FD	FD	FD	MD
Phenylhydrazine			243.5	N	N	FL	MG	FG	ML	FG	FG	MG	FD	N
VII. NITRO COMPOUNDS														
A. Aliphatic														
Nitromethane			101.2	N	N	N	FL	SD	N	FL	FD	FD	N	N
Nitroethane			114.0	N	SL	SL	FL	FD	N	FL	FD	MD	N	ML
1-Nitropropane			131.6	SL	SL	FL	FL	MD	N	FL	MD	MD	N	FL
1-Chloro-1-nitroethane			122-128	MD	FD	FD	FD	FD	MD	FD	FD	FD	SD	ML
B. Aromatic														
Nitrobenzene			210	MG	SD	MG	MD	FD	N	FD	MD	MD	MD	MD
VIII. ALDEHYDES														
Furfural			161	N	N	N	N	N	N	N	FD	FD	FL	N
Benzaldehyde			179.5	FL	SD	MD	MD	FD	N	FD	FD	FD	FD	N
n-Hexaldehyde			128.6	MG	MG	MG	MG	SD	N	N	FD	FD	N	N

n-hexadecylac

KEY
Rate of action
S—Slow
M—Moderate
F—Fast

Type of action
L—Limited swelling and/or softening
G—Gelling or unlimited swelling
D—Dissolving
N—No apparent effect

SOLVENT

IX. KETONES

Acetone
Methylethyl ketone
Diisopropyl ketone
Acetophenone
Cyclohexanone
Phorone
Mesityl oxide

Boiling point (°C, 760 mm.)	Natural pale crepe	German Buna-S	GR-2	Hycar OS-10	Butadiene- methylethylacrylate copolymer	GR-1 (Butyl)	GR-M (Neoprene)	Perbunan No. 26	Hycar OR-15	GR-P (Thiokol)	Plasticized polyvinyl chloride
56.1	N	N	N	SL	FL	N	FL	FD	FD	N	FL
80.6	FL	ML	MG	SD	FD	SL	FD	FD	FD	N	SD
123.7	FL	ML	MG	SD	FD	SL	FD	FD	FD	N	SD
202	FL	FG	SD	SD	FD	N	FD	FD	MD	FD	SD
155-157	SD	SD	MD	SD	FD	SL	FD	FD	MD	FD	SD
197.9	SD	SD	SD	FG	FD	N	MD	MD	MD	FG	FL
128	FD	FD	FD	FL	FD	FL	FD	FD	MD	N	SD

X. ESTERS

Methyl formate
Ethyl acetate
Butyl acetate
Butyl stearate
Isopropyl acetate
Ethyl oxalate
Amyl borate
Benzyl benzoate
Ethyl silicate
Ethyl acetoacetate
Triacetin
Dibutyl phthalate
Diethyl phthalate
Triethyl phosphate
Tributoxyethyl phosphate
Butylacetyl ricinoleate
Methyl methacrylate
Cottonseed oil

Boiling point (°C, 760 mm.)	Natural pale crepe	German Buna-S	GR-2	Hycar OS-10	Butadiene- methylethylacrylate copolymer	GR-1 (Butyl)	GR-M (Neoprene)	Perbunan No. 26	Hycar OR-15	GR-P (Thiokol)	Plasticized polyvinyl chloride
32.3	FL	FL	FL	FL	FG	SL	N	SD	SD	ML	N
77.1	FL	FD	FD	MD	FG	ML	MD	MD	MD	N	ML
126.3	MD	FD	FD	FL	MD	MG	MD	N	N	N	ML
220-225 (25 mm.)	FL	FG	FG	SD	FD	N	FD	FD	SD	N	FL
88.4	FL	N	N	SL	N	N	N	N	N	N	N
186.1	FD	N	SD	MG	N	FG	N	N	N	N	N
143-147 (10 mm.)	FL	SD	SD	MG	FG	N	MD	FG	MD	MD	N
323-324	FL	SD	SD	N	N	N	N	N	N	N	N
168.1	SL	ML	N	N	ML	N	N	N	FD	N	N
180.7	N	N	N	N	N	N	N	N	N	N	N
258-259	N	N	N	N	N	N	N	N	N	N	N
339.2	SL	MG	MG	MG	FG	N	MD	MG	SD	N	FL
216 (5 mm.)	MG	MG	MG	SD	SD	N	SD	SG	N	N	FL
295 (13 mm.)	N	ML	ML	ML	FL	N	ML	MG	MG	N	FL
—	SL	SL	ML	ML	FL	ML	FL	FG	N	N	ML
220-235 (4 mm.)	FL	MD	MD	MD	FL	N	MD	MD	N	MD	FL
—	FD	FD	FD	SD	FD	ML	N	SL	N	SL	FL
—	MG	MG	MG	MG	MG	N	N	N	N	N	N

ent rubbers both have the same rating FL (fast swelling) in the same solvent does not necessarily mean that corresponding vulcanizates can be expected to swell to the same degree in the same solvent. It does mean, however, that the elastomers rated FL both produce vulcanizates which normally swell less in the solvent in question than a vulcanizate made from an elastomer which is completely dissolved in the same solvent indicated by a rating of FD, MD, or SD.

In applying these data to vulcanized compounds, allowances must be made for degree of vulcanization, pigment loading, and the presence of plasticizers or softeners which may or may not be extracted by the solvent under consideration.

Thus by proper interpretation of these studies it is possible to find the answers to many practical questions which arise daily in rubber technology. The following few examples illustrate practical use of the table:

1. Q. Which solvents can be expected to serve best for the manufacture of Thiokol cements?
 - A. Dioxane, acetophenone, cyclohexanone, benzene, styrene, chloroform, 1,2-dichloroethane, and benzyl alcohol all show excellent solvent action on Thiokol.
2. Q. Which chemical group of solvents would be most practical for dissolving a vinyl resin such as is contained in Koroseal products and an acrylonitrile butadiene synthetic such as Hycar-OR or Perbunan or a blend of the two materials?
 - A. The ketones appear to be the most logical choice.
3. Q. Which general classification of plasticizers would be expected to have the greatest softening action on Hycar-OR or Perbunan?
 - A. From the action of the solvents, high-boiling, high-molecular weight esters, ketones, chlorinated hydrocarbons, and compounds containing the benzyl group should be most effective.
4. Q. Which general classification of plasticizers would be expected to have the greatest softening action on GR-S?
 - A. The solvent data indicate that the hydrocarbons in general should be most effective.
5. Q. Which of these elastomers would serve best for making a hose tube used to deliver aniline?
 - A. Interpretation of the data shows that natural rubber would serve best for this application.
6. Q. If a storage tank were to be lined with a rubbery composition to resist the action of pyridine or dioxane, which of these elastomers would serve best or be at least affected by the solvents?
 - A. The solvent data show that Butyl rubber would be expected to be least affected by either solvent.
7. Q. Which of these elastomers would serve best for compounding a gasket used to seal against carbon disulfide?
 - A. Hycar OR-15 and Koroseal products are apparently affected least by this solvent.

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[illegible]

**Nevoll
Liquid ammonia
Circo light processing oil**

EFFECT OF TEMPERATURE ON RESILIENCE *

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INTRODUCTION

The recent use of rubber components in extremes of climate and under a variety of service conditions has drawn attention to the importance of the knowledge of the physical properties of rubber vulcanizates at temperatures other than normal; the dearth of such knowledge has been emphasized by the enforced replacement of natural rubber by synthetic rubbers having reduced resistance to cold. When designing mechanical parts, the engineer must know first the conditions under which the part will be required to operate and, second, the physical properties under these conditions of the materials to be used.

In a recent review Riesing¹ has given illustrations of the importance of such knowledge; in particular he has shown that rubber mountings in an automobile may well be subjected to temperatures as high as 80 to 100° C, and although rubber mountings normally warm up during their operation, they may commence to function at extremely low temperatures, while there is a limiting temperature below which they fail even to warm up.

The first part of this paper gives the results of the measurement of rebound resilience on a number of vulcanizates over a wide range of temperatures. Resilience is one of the important physical properties of a rubber vulcanizate, and in designing parts for shock or energy absorption, data on the resilience of the material are essential; for such applications a material with a low resilience is required, but as the energy absorbed manifests itself in the form of heat, the temperature rise of the absorber may control the permissible value of the resilience. In many other applications it is necessary that the material should have a high resilience and so absorb little energy. The resilience is normally determined by measuring the rebound of a ball or pendulum after impact on a sample of rubber; various other methods have been used, involving, either measurement of the decay in amplitude of the damped free vibration which results when a sample is deformed and then released, or measurement of the energy loss during sustained forced vibrations. Unhappily, the results from one test do not always show great similarity to the results from another test and, as a result, the engineer has to rely on empirical correlations with resilience tests conducted in a particular way, or on service behavior.

The second part of this paper gives the lines along which an investigation is being conducted to illuminate the significance of these dissimilarities. The measurement of resilience over a range of temperatures has an added importance, since it throws some light on the structure of the rubber and on the processes taking place during deformation. Recent papers² which have just become available in this country show that there has been interest and activity in this field in Germany during the war years.

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PART I

THE INFLUENCE OF TEMPERATURE ON REBOUND RESILIENCE

Experimental technique.—The rebound resilience measurements which are described here were made on a pendulum instrument which was constructed from designs described by Lüpke³. The pendulum consists of a horizontal metal rod of known weight suspended by four fine fish lines so that it rebounds after falling from a fixed height and striking horizontally against a rubber sample clamped to a rigid anvil. The ratio of the rebound height to the height of fall is equal to the ratio of the energy of the pendulum after impact to the energy before impact and, when expressed as a percentage, is called the rebound resilience. The major portion of the energy lost during impact is absorbed by the rubber; however, some energy is lost by the motion of the sample and the anvil, and also there are small losses from windage. Bulgin⁴ has given a de-

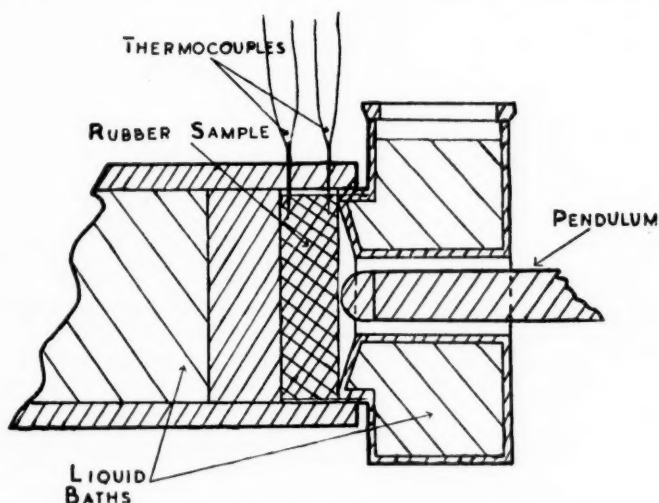


FIG. 1.—Sketch of sample holder.

tailed description of the various losses which occur in pendulum measurements; however, in the work described here it was considered that the energy losses due to the motion of the anvil and windage were small and could be neglected; the losses due to the motion of the sample were largely overcome by clamping the sample securely around its periphery with a metal ring. Results given in the second part of this paper show that these assumptions were justified, indeed, providing the sample is rigidly clamped and excessive frictional losses are avoided, stray energy losses are less than 1 per cent.

Measurements of the resilience of a number of natural and synthetic rubber vulcanizates were made over a range of both high and low temperatures. Samples of the vulcanizates 2 inches in diameter and $\frac{1}{2}$ inch thick were clamped to the anvil by means of a screw ring, and thermocouples were placed in both the front and rear of the sample, which was maintained at a constant controlled temperature for ten minutes before rebound measurements were made. A sketch of the anvil is shown in Fig. 1. The baths in front and behind the

sample were filled with water for measurements at temperatures greater than 20° C, in which case the water was heated until both thermocouples indicated the same required value of the temperature; for measurements at low temperatures the water was replaced by methyl alcohol, and powdered solid carbon dioxide was used as a source of cooling. In this way it was possible to control the temperature of the sample to $\pm 1^\circ$ C and make rebound resilience measurements over the range of temperatures -60° to 100° C.

It was observed that the sample was "mechanically conditioned" by repeated impacts and that as a result the height of rebound increased slightly during the first few successive impacts, the value of the resilience quoted here is that obtained from readings of the constant maximum value of the rebound achieved after five or six successive impacts. Repeated reference has been made in the literature to this effect, and "conditioning" of the type described here has usually been recommended before rebound measurements were made.

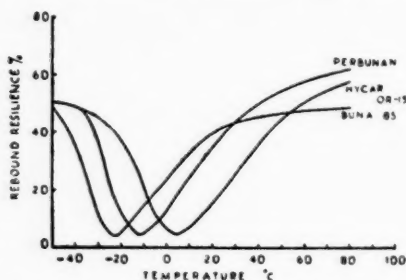


Fig. 2.—Resilience-temperature curves of butadiene and butadiene-acrylonitrile copolymers.

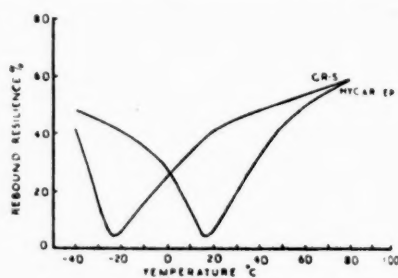


Fig. 3.—Resilience-temperature curves of butadiene-styrene copolymers

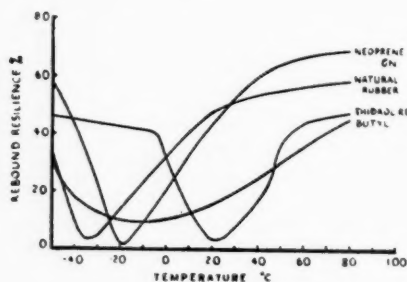


Fig. 4.—Resilience temperature curves of various rubbers.

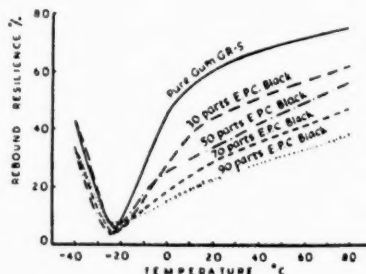


Fig. 5.—Change of resilience with black content.

The shape of resilience-temperature curves.—Typical curves showing the change of the percentage rebound resilience with temperature of various vulcanizates are given in Figures 2, 3 and 4. A study of these curves shows that the resilience is very sensitive to changes in temperature, and all the curves show the same characteristic form. The resilience has its highest value at high temperatures; as the temperature is reduced the resilience decreases steadily, and at lower temperatures there is a more rapid decrease in resilience until at a temperature characteristic of the material and of the method of test practically all of the energy of the pendulum is absorbed by the rubber during

impact. At this temperature the resilience curve passes through a minimum, and further reduction of the temperature results in an increase in the value of the resilience.

A feature of all the curves is the presence of a temperature at which the resilience has a small minimum value, and in all the rubbers (with the exception of Butyl) which were tested there is a rapid change of resilience with temperature in the neighborhood of the minimum. The resilience-temperature curve is apparently substantially symmetrical about the minimum value of the temperature, and this symmetry is maintained until low temperatures. Furthermore, there is no evidence of transition temperatures at which the dependence of resilience on temperature suddenly alters. Such transition temperatures have been reported by some authors who have worked over limited ranges of temperature. Another interesting feature is that, over a range of temperatures below the minimum, a reduction of temperature results in an increase in the resilience, and at low temperatures, the resilience may be comparatively high, and thus little energy is dissipated. This behavior readily accounts for the existence of a "barrier point", *i.e.*, a limiting temperature below which rubbers fail to warm on use.

The general shape of these resilience-temperature curves can be accounted for in a qualitative manner by the time- and temperature-dependence of the deformation of the vulcanizate. In an ideally elastic material the deformation is independent of the time under load, and completely reversible, and the energy used up in producing a deformation would all be recovered on removal of the deformation; if there were no extraneous energy losses, such a material would have a resilience of 100 per cent. However, real materials dissipate some energy during deformation; this loss of energy may be due either to true irreversible flow or to the incompleteness of recovery of some of the elastic, or recoverable, component of the deformation during the period of impact. The elastic or recoverable component of the deformation which does not reach its final value immediately, is called the high-elastic component, and it is this high-elastic component which is necessary for rubberlike behavior. As very little irreversible flow takes place during the short period deformation of vulcanized rubber, changes in the high-elastic component are responsible for the changes of resilience.

The effect of temperature on high-elasticity has been considered elsewhere⁵. When a stress is applied to rubber, the molecules depart from their random orientation, but as the molecules are not perfectly free to move, due to mutual interactions between them, and the deformation does not attain its full value immediately; on sudden removal of the stress the impressed orientation decays at a rate defined by an orientation or relaxation time; this orientation time is the time taken for the high-elastic component to recover $(1 - 1/e)$ of its value. The orientation time changes rapidly with temperature, and for rubberlike materials a tenfold decrease in orientation time may result from a change in temperature of less than 10°C . It is evident that if a force is applied and removed slowly compared with the orientation time, then the deformation can attain, or recover to, its final value almost completely and hence little energy is dissipated and the measured value of the resilience is high. However, as the orientation time is increased by lowering the temperature, the high-elastic component of the deformation produced by a similar force applied at the same rate, takes place more slowly at lower temperatures and, as a result, the deformation attained in a given time is not so large, *i.e.*, the rubber is stiffer, and the recovery in a given time is less complete; thus more energy is dissipated

during impact, and the resilience consequently decreased. This incomplete recovery is a manifestation of a phase lag between the applied force and the deformation, and it can easily be shown that for a force which varies sinusoidally with time the residual deformation at the end of the impact is linearly proportional to the energy dissipated. At very low temperatures the orientation time is so large that very little high-elastic deformation can occur during impact, and as a result most of the deformation is ideally elastic, and hence very small and completely reversible, and the resilience is again high. At some intermediate temperature at which the duration of impact is similar to the orientation time, there is a minimum value of resilience; if the force during impact varies sinusoidally with time, then the minimum occurs when the duration of the impact is approximately $\pi\tau$, where τ is the orientation time.

Some discrepancies appear when one endeavors to represent the behavior of rubber by such a simple theory, and for a more complete agreement it is necessary to consider a range of orientation times.

Discussion of the resilience properties of various vulcanizates.—The effect of temperature on the rebound resilience of polybutadiene and butadiene-acrylonitrile and butadiene-styrene copolymers is shown in Figures 2 and 3. The percentage ratio of butadiene to acrylonitrile in the copolymers Perbunan and Hycar OR-15 is 70:30 and 60:40, respectively, while the percentage ratio of butadiene to styrene in the copolymers GR-S and Hycar-EP is 75:25 and 50:50, respectively. It is evident from these curves that increased acrylonitrile or styrene content results in a raising of the temperature of the minimum in the resilience-temperature curve. This movement of the minimum to higher temperatures corresponds to an increase in (the average value of) the orientation time of the molecular segments taking part in the deformation. Such behavior can be readily forecast, as the addition of bulky or strongly polar groups to the molecules leads to their more sluggish motion under the action of applied forces. The introduction of polar groups into molecules which are not inherently polar results in increased electrostatic forces, which both oppose motion between the molecules, and cause a stiffening of the molecules as a result of interaction between polar groups attached to the same molecule, whereas bulky side chains hinder the motion of the molecules by simple mechanical intermolecular and intramolecular interference. Thus the temperature of the minimum is closely associated with the molecular structure of the material. It will be noticed that the increase of the acrylonitrile or styrene content has merely moved the resilience-temperature curves bodily to higher temperatures, i.e., if the temperature scales are altered so that the minima are coincident the various curves almost lie on top of each other. This is true in all cases except the polybutadiene compound, Buna-85, which shows a low value of resilience at high temperatures. This difference is presumably due to the fact that the source and method of preparation of Buna-85 are different from those of the copolymers. A similar explanation may account also for the similarity in the temperature of the minimum for both Buna-85 and GR-S. It is, therefore, unnecessary to introduce, as did Jones and Snyder⁶, a concept of thermosensitivity of the acrylonitrile or styrene content to explain the changes in resilience properties resulting from their introduction into the vulcanizate.

Figure 4 gives the resilience-temperature curves of some other synthetic and natural rubber vulcanizates; although all the materials tested possess a minimum value of resilience, some of them do not exhibit the sharp and well marked decrease to a minimum followed by the increase within a comparatively

small range of temperatures. The Butyl sample shows a gradual approach to the minimum over a wide range of temperatures; it has already been indicated that the low values of resilience in rubber vulcanizates which do not exhibit flow are due to a similarity in the period of deformation and the orientation time of the molecular segments, and it is evident that the behavior of the Butyl vulcanizate can be explained by a wide range of orientation times, so at even relatively high temperatures, *viz.*, widely removed from the temperature of the minimum, a considerable portion of the deformation takes place with orientation times of the same order as the period of the deformation. The following data taken from the Butyl and the natural-rubber curves illustrate this wide dispersion.

Butyl	Resilience 8 per cent at minimum (-20°C) Resilience 20 per cent at $+35^{\circ}\text{C}$
Natural rubber	Resilience 5 per cent at minimum (-35°C) Resilience 46 per cent at $+20^{\circ}\text{C}$

This comparatively wide dispersion of orientation times is responsible for the sluggish behavior of Butyl vulcanizates; for example, normal tensile-set measurements which were taken after dumbbell samples had been extended by 200 per cent of their original length for fifteen minutes and then allowed to recover for one hour, confirm that Butyl vulcanizates recover slowly and suggest that they show more truly irreversible flow than normal rubbers.

Tensile set: Butyl, 25 per cent; natural rubber, 6 per cent

The behavior of the Butyl vulcanizate can be contrasted with the behavior of Thiokol-RD, both of which show low resilience values at relatively high temperatures. In the case of Butyl this is due to a wide dispersion of orientation times, but Thiokol-RD shows the more normal type of curve, with a well marked minimum, the high temperature of the minimum being due to the very polar nature of Thiokol-RD and the consequent lack of mobility of its molecular segments.

Previous authors who have studied the resilience properties of Butyl and Thiokol-RD have suggested that these two rubbers possess peculiar resilience properties. The results in Figure 4, however, show that they exhibit the same general type of behavior characteristic of other rubberlike materials.

The effect of various proportions of carbon black in a GR-S stock is shown in Figure 5; these curves show that, although the increased proportions of black result in a decrease in the value of the resilience, very little change is caused either in the nature of the minimum or to its temperature. Table I gives resilience data which have been taken from measurements on GR-S vulcanizates compounded with various types of black. The Table includes also resilience data of vulcanizates which include various extenders, plasticizers, and fillers. The freeze point determined by a torsion modulus method is given in the third column of the Table, the freeze point is defined as the temperature at which the modulus is ten times its value of 0°C .

Although it is important that resilience measurements should be made over a wide range of temperatures before adequate comparisons of the behavior of different rubbers can be made, it will be seen from Table I that to obtain comparative data of the effect of compounding ingredients on the resilience properties it is sufficient to make measurements at only a few temperatures. The addition of plasticizers or extenders to the stock is capable of

TABLE I

GR-S Mixing	Temperature of minimum resilience (°C)	Freeze point (°C)	Rebound resilience (percentage)				
			At -20° C	0° C	20° C	50° C	80° C
Pure gum	-25	—	8	45	61	69	74
+ 50 parts M.T. black	-25	-49	8	36	58	64	69
+ 50 parts E.P.C. black	-25	-48	7	26	42	51	61
+ 50 parts M.P.C. black	-28	—	14	31	42	47	49
+ 50 parts C.C. (Shaw- inigan) black	-26	—	12	31	44	51	54
+ 50 parts C.C. (Spheron- N) black	-27	—	17	29	35	39	40
+ 50 parts lampblack	-27	—	12	43	46	62	63
+ 50 parts E.P.C. black with replacement by 25 pts. extender	-30	-48	10	22	33	42	46
+ 50 parts E.P.C. black with replacement by 20 parts Okerin wax	-20	-47	8	22	36	50	60
+ 80 parts activated CaCO ₃ and 25 parts coumarone resin	-22	-41.5	3	20	40	51	56

producing a pronounced shift of the minimum, since the value of the orientation time depends on the viscosity of the medium in which the molecules are forced to move. This is well illustrated in Figure 6, which shows the effect of

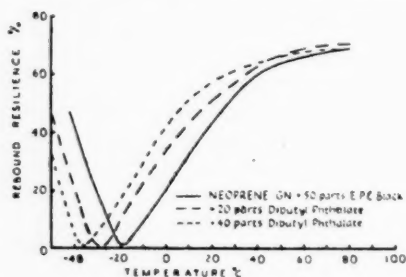


Fig. 6.—Effect of dibutyl phthalate on resilience temperature curves of Neoprene GN.

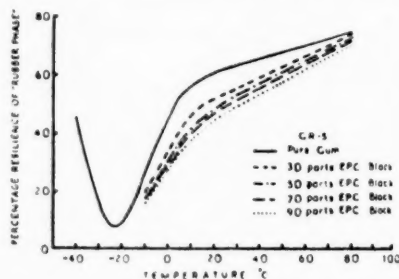


Fig. 7.—Effect of black content on resilience of "rubber phase".

dibutyl phthalate in a Neoprene-GN black vulcanizate; the resilience-temperature curve is translated to lower temperatures with increasing amounts of dibutyl phthalate. The plasticizer presumably penetrates between the rubber molecules and both causes their separation, and because of the mutual attraction between the plasticizer and the rubber molecules neutralizes the polar groups, and hence causes a reduction in the forces between the molecules and permits more freedom of motion. This should be contrasted with the effect of carbon black and fillers; in these cases the minimum is not shifted to lower temperatures, although the compounding ingredients must act as a volume diluent. This suggests that the particle size of the materials preclude their free penetration between the rubber molecules and the average forces between the rubber molecules are not greatly affected by the inclusion of carbon black, whereas the low molecular-weight plasticizer is capable of flowing between the rubber molecules.

However, it is known that carbon black or filler particles must perturb the stresses and strains experienced in the body of the rubber, and as a result may cause reinforcement. To reconcile these apparently opposing phenomena, it is suggested that zones of rubber exist between the black particles and agglomerations of black particles; these zones are of such a size that the mobility of the rubber molecules in any zone is only slightly affected by the presence of the black.

The decrease in the value of the resilience due to the addition of carbon black must, then, be attributed to the energy absorption taking place in two distinct phases; one is due to frictional losses between the carbon particles; the other to the incomplete recovery of the deformation of the rubber molecules. Compared with the temperature-sensitive losses due to the rubber, the losses due to carbon black can be assumed to be independent of temperature. These ideas obviously represent a considerable simplification of the actual processes, but an analysis on these lines of the data given in Figure 5 is shown in Figure 7. Here the energy absorbed by the rubber phase of each vulcanizate has been obtained by extrapolating the resilience curves to higher temperatures when it was assumed no energy was absorbed by the rubber phase. The resulting curves, which show the change of energy absorption of the rubber phase with temperature, are not in very good agreement, although they suggest that the ideas are not without foundation. The addition of carbon black besides causing frictional losses in the carbon black phase also results in a wider dispersion of the values of the orientation time.

The resilience-temperature curves of GR-S vulcanizates, unlike most of the other rubbers tested, can be extrapolated only with some guessing, since they do not give much evidence of becoming asymptotic to a particular value of resilience in the temperature range considered. This is presumably due to a wide dispersion of orientation times being already present in GR-S before the addition of black.

In some applications it is advantageous to use mixtures of synthetic rubbers or of natural and synthetic rubbers to produce a vulcanizate whose physical properties are intermediate between those of the original components. For example, it may be necessary to produce a vulcanizate which gives a certain known swelling under particular service conditions, in which case a mixture of a rubber which is resistant to swelling and one which swells more freely is indicated. Alternatively, a mixture of rubbers may overcome some processing difficulties, *e.g.*, allow easier handling on the mill, or result in less shrinkage in open-steam cure, or in the mould (natural rubber is added to Thiokol-A for this purpose). Figure 8 demonstrates a fundamental difference between the

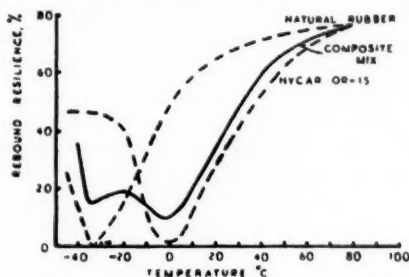


FIG. 8.—Effect on resilience of compounding two rubbers together.

behavior of mixtures of rubbers, and rubbers having the same overall composition but produced by copolymerizing the two ingredients into one molecule. It shows resilience-temperature curves for natural rubber, Hycar OR-15, and a third vulcanizate containing equal parts of each of these; the full line corresponds to the mixture of rubbers and the dotted lines to the individual rubbers. The curves indicate that both rubbers can be considered to exist separately in the composite mix; as the temperature is decreased, the resilience of the Hycar OR-15 component of the composite mix goes through a minimum; this minimum is followed by an increase in resilience corresponding to the increase of resilience of the Hycar OR-15 component at temperatures below 0° C, then there is a second minimum corresponding to the natural rubber component. Thus for a mixture of rubbers, poor resilience properties should be evident at temperatures below and including the temperatures at which poor resilience is exhibited by one of the rubbers. Modification of the chemical structure of the molecule by copolymerization, however, merely results in a bodily shift of the resilience-temperature curves (see Figures 2 and 3).

It has been shown that the shape of the resilience-temperature curves can be accounted for by ideas of orientation times, and that the curves possess a minimum when the period of deformation is similar to the orientation time; high temperatures correspond to short orientation times and low temperatures to long ones. The different instruments which have been used to determine resilience give different periods of deformation and so the resilience data obtained depend on the instruments used; with instruments possessing long periods of deformation the curve has minima at low temperatures, whereas with instruments possessing a shorter period the minima occurs at higher temperatures.

Rebound resilience measurements on a number of vulcanizates with various periods of impact illustrate this displacement of the resilience-temperature curves. The rebound of balls of various sizes, ranging from 0.5 to 10 grams, dropping from various heights, showed displacement of the minima, in extreme cases of over 10° C. As it requires considerable changes in the nature of the impact to cause an appreciable difference in the resilience curves, it would appear that all instruments which possess periods of impact which are of the same order give results which, although not strictly comparable, are very similar.

However, it is shown in the second part of this paper that, although all pendulum instruments which are in general use possess periods of impact which are not widely dissimilar, *i.e.*, periods between 1/500 and 1/10 seconds, the results may possess strong resemblance only at temperatures higher than the minimum; at temperatures below, and in the immediate neighborhood of the minimum, the measured values of the resilience on different instruments may be widely at variance. These discrepancies are ascribed to violent vibrations of the pendulum and are discussed later.

Further analysis of the results.—Simple considerations of the sort which have been developed so far involving the concept of orientation times are sufficient to suggest the processes which give rise to the behavior which has been discussed, but they are obviously not adequate to represent in any detail the complex behavior of rubberlike materials, and it is necessary to use more elaborate theories. A brief survey of the various approaches which have been adopted to assist in a more complete description of rubberlike properties is not out of place here.

Although the behavior of rubberlike materials cannot be represented by the classical theories of elasticity and viscosity, Maxwell and others have shown that the behavior of materials with complicated structures can often be represented by the superposition of elastic and viscous behavior. Various mechanical models and electrical analogies which illustrate the behavior of rubberlike materials have been put forward. These models consist of two types of elementary systems, (1) perfectly elastic elements (springs) and (2) Newtonian viscous elements (dashpots); the superposition of two such elements in series forms a single Maxwell element, and composite models possessing several such elements in series and parallel which adequately represent the observed macroscopic behavior can be constructed. However, the meaning given to the springs and dashpots does not necessarily correspond to distinct phases of elastic and viscous elements in the materials being considered. An alternative to the construction of models is to represent the behavior by a mathematical relationship, and Alexandrov and Lazurkin⁷ have suggested such a relation for rubberlike polymers which has been used with some considerable success over limited ranges. In this relationship the high-elastic component of the deformation is represented by a simple exponential dependence on time; and Moyal⁸ has constructed a mechanical model which gives the suggested relationship between deformation and time. Refinements involving several exponentials with different relaxation times are necessary before very close agreement between theory and practice is obtained.

Deeper insight into the structure of the materials and their behavior has been obtained by an extension of the analysis from a treatment of macroscopic behavior alone to a consideration of the molecular processes, basing explanations on concepts of the orientation of molecules or molecular segments, their rotation being hindered by Van der Waals forces. Debye⁹ has had considerable success in accounting for electrical properties in this way. But no matter whether macroscopic or molecular models are used, both treatments can account for the time dependence of the high-elastic component of the deformation, and equations involving one or more orientation or relaxation times can be derived.

It has long been realized that the majority of rubberlike behavior is due to thermal motion, and a kinetic theory of high elasticity which recognizes this has been formulated. High elasticity, which is peculiar to molecules with long molecular chains, is accounted for by the continuous thermal motions of the molecules, their most probable position being controlled by thermal motions and mutual interactions between molecules. The behavior of the large number of molecules cannot be observed or measured, but it is possible to measure certain thermodynamic quantities which give a simple interpretation of the observed behavior. On the application of a force, molecules which are not perfectly free to move are deformed, but do not reach a final position immediately, owing to inter- and intramolecular actions, and they pass from a disordered probable state to a more ordered less probable state, and the main problem in treating a large number of molecules is to assess the degree of order or disorder existing; or in thermodynamical terms the entropy function, which corresponds to the probability of a particular state.

In long-chain compounds the deformation is generally due to the motion of molecular segments, not of whole molecules. Not all these segments possess the same thermal kinetic energy, and their energies are distributed over a wide range; but at any temperature there is a probability that a particular segment

of a molecule possesses an energy which enables it to break the bonds holding it in place and move from one equilibrium position to another. The probability that a molecule would migrate from one position to another is given by $Ae^{-Q/RT}$. Here Q is called the energy of activation, and represents the height of the potential barrier which the molecule must cross and is expressed in calories per gram molecule. Under the action of an applied stress the normal random motion of the molecules takes place preferentially in the direction of the stress and a macroscopic deformation results. The rate of deformation of rubber is very sensitive to temperature changes, and a rate process of the type given in the equation above appears to adequately represent this dependence.

TABLE II

Rubber	Freeze point (° C)	Resilience minimum (° C)	Power-factor maximum (° C)	B-A (° C)	C-B (° C)
	A	B	C		
Perbunan	-34	-10	21	24	31
Hycar OR-15	-23	3	30	20	27
Hycar-EP	-16	18	45	32	27
Neoprene-GN	-41	-15	≈ 5	26	≈ 20
Thiokol-RD	-11	22	52	31	30

There are very strong similarities between the processes of electrical and mechanical energy absorption, and both show a maximum at a temperature at which the period of the applied field or force is similar to the orientation time of the molecular segments which take part in the processes. Table II includes data on the freeze point, the temperature of the minimum in the rebound-resilience curve, and the temperature of the maximum in the power factor ($\tan \delta$) curve (both of the last two temperatures correspond to maximum energy absorption). Measurements of the power factor were made at 10^6 cycles second.

The fifth and sixth columns of the table give the differences between the temperatures of the resilience minimum and the freeze point and the power factor maximum and the resilience minimum. These differences are reasonably constant for all the rubbers for which power factor data were available, and they give weight to the assumption that similar molecular processes are the controlling factors in stiffness, resilience, and electrical energy absorption.

The differences in the fifth and sixth columns can be accounted for, as explained above, by differences in the period of application of the forces responsible for the deformations; these periods are: 20 seconds in the modulus test, about 20 milliseconds in the rebound resilience test, and 1 microsecond in the power factor test.

The similarities are shown very clearly in Figure 9, which gives the change of modulus, rebound resilience, and power factor with temperature for a Hycar OR-15 vulcanizate. This series of curves is typical; Hycar OR-15 was selected for this illustration because limitations of the thermostatically controlled chamber in which electrical measurements were made precluded measurements at temperatures much below 10°C , and it was therefore necessary to select a vulcanizate showing a maximum value of power factor at a temperature considerably higher than 10°C . Although close parallels obviously exist the similarities between mechanical and electrical energy absorption can be overemphasized. In resilience measurements all rubbers exhibit temperatures at which there is considerable energy absorption, whereas in electrical measurements non-polar rubbers show little energy absorption over the whole temperature range.

A considerable amount of work has been performed on the analysis of power factor-temperature curves, and working hypotheses have been formulated involving either orientation times or the theory of absolute reaction rates.

However, rebound resilience data are not so tractable mathematically and present a much more complex problem.

It has been shown that the energy absorbed is strongly dependent on temperature, and this suggests that the physical nature of the energy losses can be investigated by applying equations of chemical unimolecular reactions. To do this it is necessary to adopt some assumptions.

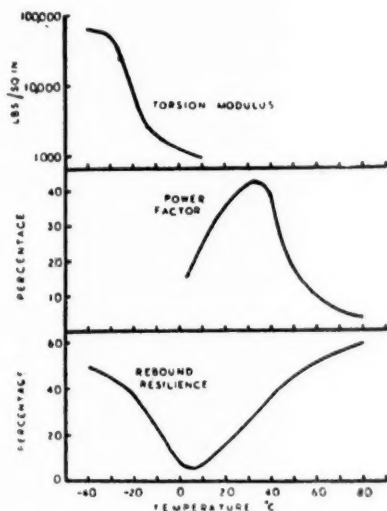


Fig. 9.—Similarities between electrical and mechanical properties of Hycar OR-15

First it is assumed that the losses are due entirely to the incomplete recovery of the high-elastic component of the deformation, and thus the resilience R is given by the following relation:

$$R = \left(1 - \frac{\oint F \cdot dD_{H.E.}}{\int_0^{D_{max}} F \cdot dD} \right) \times 100\%$$

Here D is the deformation at any instant t produced by the force F and $D_{H.E.}$ is the high-elastic component of the deformation.

Secondly it is assumed that the forces exerted on the rubber during the impact vary sinusoidally with time. Results given in the following part of this paper indicate that this assumption, although not completely true, should be valuable in giving results of a semiquantitative nature.

Further, it is assumed that the high-elastic component of deformation produced by a constant force F can be represented by:

$$D_{H.E.} = F\alpha(1 - e^{-t/\tau}) \quad (1)$$

or for a sinusoidal force $F_0 \sin \omega t$:

$$D_{H.E.} = \text{Imaginary part of } F_0 \alpha \frac{(e^{i\omega t})}{1 + i\omega\tau} = \frac{F_0 \alpha}{1 + \omega^2 \tau^2} (\sin \omega t - \omega \tau \cos \omega t)$$

Then the energy lost during impact is:

$$\oint F \cdot dD_{H.E.} = \frac{F_0^2 \alpha}{1 + \omega^2 \tau^2} \int_0^{\pi/\omega} (\omega \cos \omega t + \omega^2 \tau \sin \omega t) \sin \omega t \cdot dt$$

$$= \frac{F_0^2 \alpha}{2} \cdot \frac{\pi \omega \tau}{1 + \omega^2 \tau^2} \quad (2)$$

This energy loss is a maximum when $\omega \tau = 1$; hence the resilience is a minimum when the period of indentation is $\pi \tau$, and the ratio of the energy absorbed at any temperature to the maximum energy absorbed is:

$$\frac{\oint F \cdot dD_{H.E.}}{\oint_{\max} F \cdot dD_{H.E.}} = \frac{1 - R}{1 - R_{\min}} = \frac{2\omega\tau}{1 + \omega^2 \tau^2} \quad (3)$$

This is similar to the familiar relation obtained by Debye for the dependence of dielectric constants and power losses on frequency and temperature, but the energy losses during impact are not describable by a simple Debye mechanism. Values of $\log \omega \tau$ obtained from equation (3) for a number of rubbers are shown plotted against the reciprocal of the absolute temperature T in Figure 10.

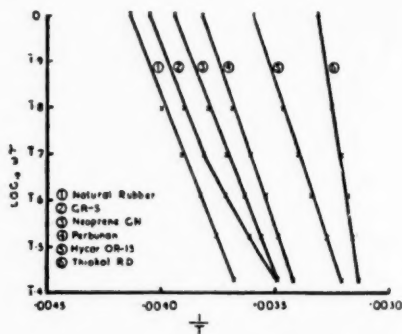


FIG. 10.—Logarithmic dependence of orientation time on absolute temperature.

The values of $\log \omega \tau$ have been obtained from the curves shown in Figures 2, 3 and 4 over a range of temperatures in the neighborhood of the minimum; these data were obtained on black vulcanizates but the suggested correction for the energy losses due to the black was applied before the values of $\log \omega \tau$ were calculated. The data show that $\log \omega \tau$ has an approximately linear dependence on $1/T$ (there is very good agreement in all data shown except for the GR-S vulcanizate) and confirm that the variation of $\omega \tau$ with temperature can be represented by the rate equation:

$$\omega \tau = A e^{-Q/RT}$$

The value of ω only varies slightly with temperature over the temperature ranges considered, and the gradients of the straight lines give values of Q which can be considered as the apparent free energy of activation for the processes which occur during the deformation.

The values of Q obtained in this way for all the rubbers tested lie between 3 (Butyl) and 15 (Thiokol-RD) K. cal. per g.-mol. the value for natural rubber and most synthetics is about 6 K. cal. per g.-mol.

Although these values of Q should be treated with some reserve, they emphasize the great similarity between the shape of the resilience-temperature curves for all the rubbers tested except Butyl and perhaps Thiokol-RD. The low Q value obtained for Butyl corresponds to a low energy barrier opposing motion and hence relative insensitivity of resilience, and other properties, to change of temperature. Correspondingly the high Q value obtained for Thiokol-RD corresponds to a high energy barrier and a rapid change of resilience properties with temperature.

Q values have been obtained also from electrical measurements of the power loss on some pure gum vulcanizates; the values of Q obtained from electrical measurements are of the same order as those from resilience measurements, and are similar also to the values of the energies of activation for viscous flow (10 to 15 K. cal. per g.-mol.) which have been quoted in the literature for various unvulcanized rubbers. Although the analysis used to derive the values of Q is not based on arguments involving molecular mechanisms, this similarity in Q values suggests that the molecular units which take part in the readjustments in high-elastic, and electrical deformations, and viscous flow are similar.

However, it is doubtful what exact significance should be attributed to the value of Q ; as the deformation of rubber is not describable in terms of a single orientation time, the value of τ is the most probable value of a distribution of orientation times, and this distribution changes with alteration of temperature.

Before rebound-resilience data can be interpreted fully, it is essential to know more about the treatment to which the rubber is subjected during the test. An apparatus which is described in the following part of this paper has been developed to provide this information.

PART II

THE BEHAVIOR OF RUBBER DURING IMPACT

The piezoelectric pendulum.—In the investigation and the analysis of the dynamic behavior of rubber vulcanizates, various instruments involving the use of springs and mirrors have been devised, but the most accurate instrument available for studying transient or rapidly fluctuating phenomena involves the use of a cathode-ray oscillograph. To use the cathode ray oscillograph to investigate the nature of the forces and the resulting strains to which a rubber sample is subjected during the impact of the pendulum, it is necessary that one or both of these effects should be converted into voltages which are sufficiently large to give reasonable deflections of the oscillograph beam. In this work the piezoelectric effect has been used to provide the connection between force and voltage.

When certain crystals are subjected to stresses they develop electric charges. The magnitude of these charges is proportional to the applied force, and if they are supplied to a condenser a voltage given by the relation: Charge = voltage \times capacitance, is developed across the condenser.

The charge given by such crystals, *i.e.*, quartz, tourmaline, rochelle salt, is comparatively small, so the voltage has to be amplified before reasonably large deflections of the beam of the cathode ray are produced.

The apparatus which has been constructed and used to study the behavior of rubber during rebound-resilience measurements is a compound pendulum. It consists of a rigid rod with a piezoelectric gauge mounted at its center of percussion. A sketch of the gauge is shown in Figure 11. On the impact of the

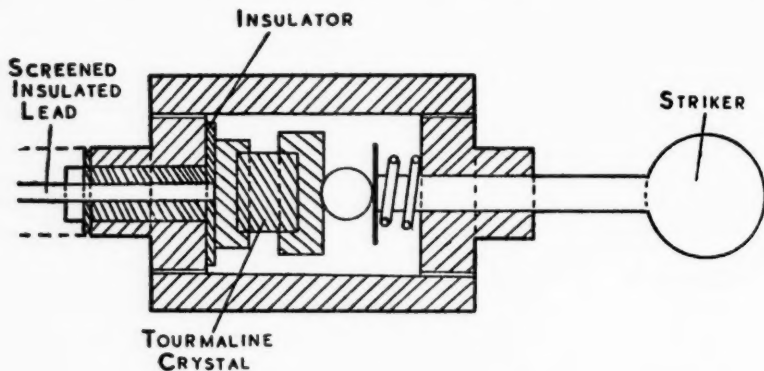


Fig. 11.—Sketch of piezo-electric gauge.

spherical bob against the rubber the thrusts exerted on the bob are transmitted through a horizontal piston rod to an earthed electrode of a tourmaline crystal, which is mounted between two brass cup electrodes, one of which is earthed to the body of the gauge and the other insulated. The charge developed on the crystal during impact is conducted through an insulated screened lead to a condenser of known capacitance and the resultant voltage change is then fed into an amplifier with a very good low-frequency response, and the amplified voltage used to deflect one beam of a double beam oscillograph.

Stationary photographs of the single traverse of the beams across the tube have been taken; the deflection produced by the force developed during impact being imposed on one beam of a double beam oscillograph and an 800 cycle timer on the other. An annotated reproduction of one of the photographs is shown in Figure 12. In order that the force record should always be obtained in the center of the single sweep of the cathode ray beam, a photoelectric device was constructed; this enabled the single sweep of the cathode ray beam to be operated by the shadow cast by the falling pendulum.

Figure 12 shows also the trace of three alternating potentials of known and graded magnitude which were applied to the input condenser immediately before each experiment and which are necessary for the interpretation of deflections on the photograph in terms of force. The piezoelectric crystal was first calibrated by comparing the deflection produced by the removal of a

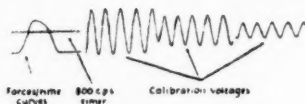


Fig. 12.—Typical record of forces during impact.

known dead load from the crystal and the deflection produced by the three known alternating potentials, the sensitivity of the crystal obtained in this way was expressed in micro-Coulombs/megadyne or for given input capacitance in millivolts/megadyne. A graph of the voltage input against deflection obtained from the three potentials in Figure 12 could thus be interpreted as a force-deflection graph and consequently deflections of the recorded impact curve read off in terms of megadynes. The deflections of the impact curve were measured with a travelling microscope at frequent intervals along the time axis; the period, after the initial contact of the pendulum and the rubber, corresponding to these observations was determined by measurements of the 800 cycle timer. Force-time curves constructed in this way from records obtained from a GR-S black vulcanizate at various temperatures are shown in Figure 13. Further analysis enabled the velocity of the pendulum bob and its indentation at any instant during impact to be determined, Figure 14 gives the force-indentation curves computed from the data shown in Figure 13. The complete

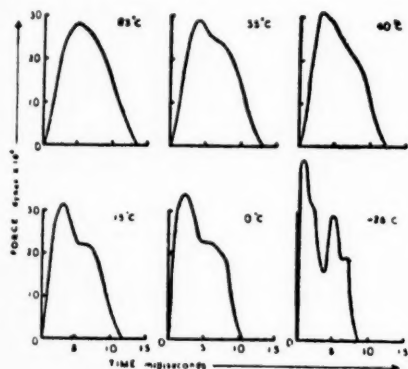


FIG. 13.—Force-time curves for GR-S.

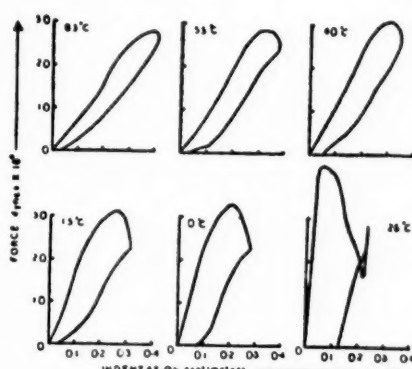


FIG. 14.—Force-indentation curves for GR-S.

force-time, velocity time, and indentation-time curves obtained from the record at 15° C are shown in Figure 15; for convenience the change in direction of velocity on rebound has not been shown.

Analysis of force-time curves.—If F is the force exerted on the bob of the pendulum of total mass M , at any instant t after the start of impact, and w the angular velocity of the rigid pendulum and v the linear velocity of the bob which is a distance k from the axis (k = radius of gyration of the pendulum), then

$$F = -Mk \, dw/dt$$

$$F = -M \, dv/dt$$

At any instant $t = t^1$

$$\int_{t=0}^{t=t^1} \frac{F}{M} dt = - \int_{t=0}^{t=t^1} \frac{dx}{dt} \cdot dt \quad V_0 - V_{t^1} = \int_{t=0}^{t=t^1} \frac{F}{M} dt$$

Here V_0 is the velocity of the pendulum bob immediately before impact, and integration of the force-time curve enables the velocity at any instant during impact to be calculated. Further integration of the velocity time

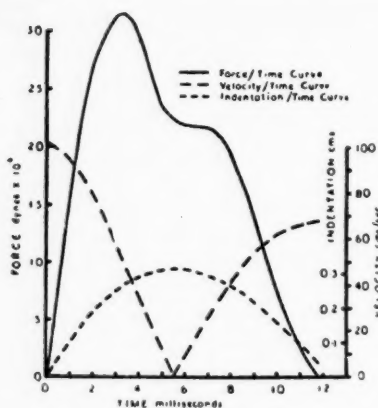


Fig. 15.—Analysis of force-time curve.

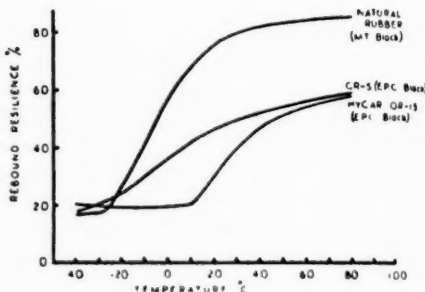


Fig. 16.—Resilience-temperature curves determined on compound pendulum.

curve gives:

$$(\text{Indentation})_1 = \int_{t=0}^{t=t^1} v dt$$

These data can be replotted as a force-indentation curve as in Figure 14. These curves are familiar hysteresis loops.

The value of the resilience can be calculated from either:

(1) The ratio of squares of the velocities before and after impact (see Figure 15).

(2) The ratio of the areas under the force-indentation curve during recovery and during indentation (Figure 14).

In the work reported here, calculations of the resilience were made by both these methods and further checked by measuring the rebound of the pendulum.

The standard deviation of the rebound resilience results used to illustrate Part II of this Report (21 in number) and determined by each of these methods was less than 2 per cent.

One feature common to some of these records is worthy of note here; the force-time records do not generally show a steady increase of force with time to a maximum value followed by a steady decay, but show undulations. Analysis of these undulations, using Timoshenko's analysis¹⁰, has shown that they correspond to transverse vibrations of the rigid pendulum rod; these vibrations are set up on the first contact of the pendulum and the rubber sample, and their amplitude is large when hard samples are used and small with soft samples. This change in amplitude of vibration with hardness of the rubber sample is clearly shown in records taken on one sample over a range of temperatures; the rapid growth of stress which is associated with hard samples causes more violent vibrations in the pendulum rod.

Such vibrations must occur in all apparatus employing a compound pendulum, and they make analysis of the behavior of the rubber during impact much more difficult.

Energy absorption at low temperatures.—The behavior of a number of vulcanizates during impact has been investigated with this pendulum; Figure 16 shows some of the resilience-temperature curves obtained. It is immediately evident that, although these curves show the expected decrease in resilience

as the temperature is lowered from high temperatures, they do not exhibit the well marked minimum and symmetry about a particular temperature which were characteristics of the curves discussed in Part I. An explanation for this unexpected behavior becomes apparent after a study of the force-time curves at various temperatures (a typical family of such curves for a GR-S vulcanizate has already been given in Figure 13); it was pointed out that at low temperatures, in the neighborhood of the temperature at which the minimum was expected, the force-time curves alter from the continuous smooth application and removal of the force, and show undulations which have a frequency characteristic of the pendulum. These undulations are caused by vibrations in the rigid bar of the pendulum, and occur when the pendulum is arrested suddenly, as a result of the rubber being stiff; at low temperatures the vibrations are of considerable magnitude and peak values of the force many times the normal maximum value have been recorded. The force during impact is now applied in a series of pulses, the period of the pulses being the same as those in the pendulum bar; as the rubber becomes progressively stiffer other natural vibrations of the bar appear, these are of a still higher frequency, and the force-time curve possesses elements of these two effects superimposed on the original.

The normal effect of an increase in the frequency of application of the force is a shift of the resilience-temperature curves to higher temperatures; thus in the compound pendulum the presence of vibrations causes the measured value of the resilience to be as if the resilience curve had been moved progressively to higher temperatures, and as a result no true minimum with a low value of resilience is observed. Another effect resulting from the large amplitude vibrations of the pendulum also comes into play; during recovery after maximum indentation the rubber returns energy to the pendulum, but the large amplitude vibrations with a period shorter than the time of recovery cause the pendulum bob to leave the rubber earlier than it would if the vibrations were absent; consequently the rubber has not adequate time to return the energy available, and at low temperatures there is a low value of resilience.

An explanation of this is that, at any instant during recovery, the velocity of the pendulum comprises the normal rebound velocity due to the return of energy by the rubber,⁵ combined with a damped velocity, which varies sinusoidally with time, which results from the vibration of the pendulum; thus during the time when the rebound velocity is enhanced the pendulum may leave the rubber earlier than it would if the vibrations were absent. If the vibrations are violent and the period of the vibrations is comparatively short, then the pendulum always leaves the rubber early; the maximum reduction in the period of recovery is, however, always less than the period of the main vibrations. Although it is possible that the pendulum may make repeated contacts during recovery if the vibrations are sufficiently violent, no records of such behavior have yet been recorded, and this behavior will not be considered here. If the vibrations are of high frequency then the reduction of the period of impact due to them will be small. Figure 19 shows the rapid decrease in the period of recovery as low temperatures are reached; at high temperatures it shows only little variation with temperature and is approximately equal to the period of actual indentation, *i.e.*, the duration of impact up to maximum indentation.

Analytically, the sum of these two effects is rather indeterminate, but an analysis on lines similar to that conducted in Section 1, except that the force is assumed to be the sum of two sinusoidal components of different periods and amplitudes, confirms the general nature of the conclusions above.

It now remains to consider the effect of vibrations on the resilience measured by other methods. In the Lüpke pendulum there are no vibrations of consequence from the fine fish line supports; however, there is a shock wave which travels along the striker. This has a very high frequency and apparently does not affect the measured value of resilience so severely. It has been observed that the resilience measured by the Lüpke pendulum assumes an approximately constant value of about 50 per cent at low temperatures. This departure from symmetry about the temperature of the minimum is ascribed to both an increased energy absorption due to violent vibrations of the striker and to the change in the physical nature of the rubber at low temperatures.

To confirm these suggestions more completely, resilience-temperature curves were determined by three very different impact methods on the same vulcanizates. Figure 17 gives these curves measured on a Hycar OR-15 vulcanizate

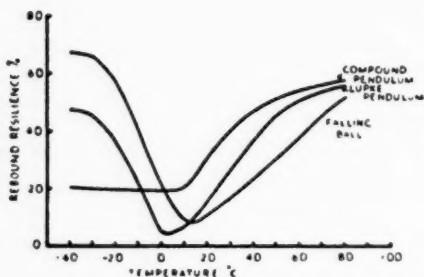


FIG. 17.—Resilience temperature curves of tests of various instruments.

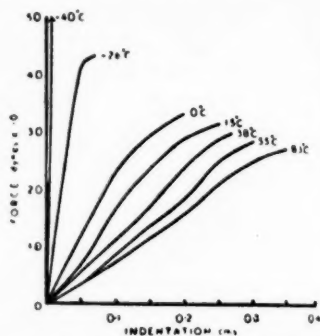


FIG. 18.—Force-indentation curves for GR-S.

by the compound pendulum, the Lüpke pendulum, and a falling-ball apparatus (in this apparatus the rebound of a steel ball of weight 1 gram falling from a height of 25 cm. was measured). The general nature of these curves at high temperatures is in keeping with the ideas forwarded in Part I, the periods of impact decreasing in the following order: compound pendulum, Lüpke pendulum, falling ball. At low temperatures, the falling-ball curve shows the expected behavior with symmetry about the temperature of the minimum and a very high resilience corresponding to the solid state at very low temperatures, the compound pendulum shows high energy absorption, and hence low resilience, as soon as the rubber stiffens sufficiently to cause violent vibrations, whereas the Lüpke pendulum shows behavior intermediate between the two. It thus appears that resilience measurements determined at temperatures where the rubber has already shown considerable stiffening should be treated circumspectly, and that a compound pendulum should not be used if fundamental information is required at such temperatures. It will be noted also that the steel ball with a small period of impact produces a minimum at a temperature higher than that for the pendulum.

The change of other impact conditions with temperature.—The illustrations used in this last section are of data obtained from the force-time curves shown earlier in Figure 13, for a GR-S black vulcanizate. Similar data have been obtained on natural rubber, Hycar OR-15, Butyl and Thiokol-RD vulcanizates, the only difference being of degree rather than of a fundamental nature.

The change of force with indentation at a number of temperatures is shown in Figure 18; this shows clearly the stiffening as the temperature is reduced. The gradient of these force-indentation curves is a function of the "dynamic modulus". Although Scott¹¹ has shown that it is possible to relate the force and the static indentation produced by a spherical ball and the "static modulus", the relation between the gradient of the force-indentation curves and the "dynamic modulus" is obscure, owing to the complex distribution of stresses in the rubber resulting from using a spherical ball as an indenter, and the frequency of the applied blow constantly altering at low temperatures. The best that can be said is that the change in the gradient of the force-indentation curves with the temperature gives some indication of the change of the "dynamic modulus" with temperature, and the stiffness increases rapidly with decrease of temperature at temperatures at which the resilience is low.

The last two figures give data of the change with temperature of some of the conditions attending impact. Figure 19 gives the change of the period of

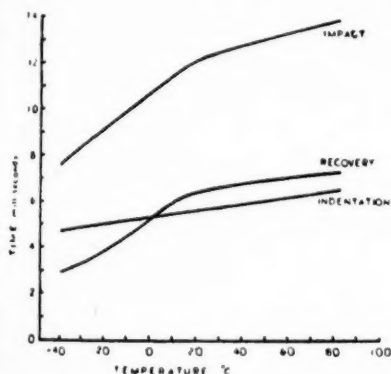


Fig. 19.—Effect of temperature on periods of impact, indentation, and recovery.

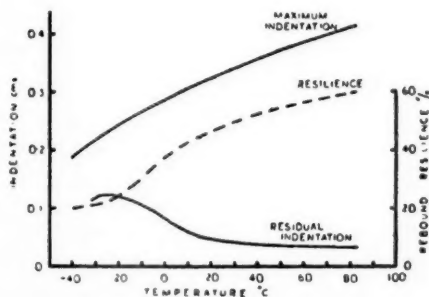


Fig. 20.—Change of indentation and resilience with temperature.

impact, and also its two component parts the periods of indentation and recovery. The rapid change of the period of recovery at low temperatures compared with the period of indentation has been discussed, and attributed to violent vibrations of the pendulum. Figure 20 gives the change of the maximum indentation, and the residual indentation, or "set", remaining at the end of impact. The decrease of the maximum indentation with temperature is due to the reduction of the high-elastic component of the deformation, which it is possible to achieve during the period of indentation, as the temperature is lowered; the increase in the residual indentation to a maximum value as the temperature is lowered is also in keeping with the ideas put forward in the general discussion in Part I. An analysis on the simple lines used in Part I shows that residual indentation should be proportional to the energy absorbed by the rubber, and so the residual indentation curve should be proportional to an inverse resilience curve; thus in the absence of vibrations it should have a maximum value at the same temperature as the minimum in the resilience, and although the behavior illustrated in Figure 20 is complicated by the presence of vibrations, some agreement is shown. It is of interest to compare the data shown in Figure 20 with the change of Conant and Liska's creep factor¹² with temperature.

COMPOUNDING DETAILS

Ingredient	Hycar OR-			Type of rubber					
	Perbunan	15	Buna-S5	GR-S	Hycar-EP	Neoprene-GN	Natural rubber	Thiokol-RD	Butyl
Elastomer	100	100	100	100	100	100	100	100	100
Carbon black	50	50	50	50	50	50	50	50	100
Zinc oxide	5	5	3	3	3	5	5	5	50
Light calcined magnesia	—	—	—	—	—	4	—	—	5
Stearic acid	0.5	0.5	2	2	2	2.5	2.5	0.5	—
Pine tar	—	—	2	3	3	—	4.5	—	3
Dibutyl phthalate	10	10	—	—	—	2.5	—	10	—
Tricresyl phosphate	—	—	—	—	—	—	—	—	—
Mercaptobenzothiazole	—	—	1.0	1	1	—	0.8	—	—
Benzothiazoyl disulfide	1.5	1.5	—	—	—	—	—	—	—
Diphenylguanide	—	—	0.25	0.25	0.25	—	—	1.5	—
Tetramethylthiuram disulfide	—	—	—	—	—	—	—	—	—
Zinc diethyldithiocarbamate	—	—	—	—	—	—	—	—	1
Sulfur	1.5	1.5	1.5	2	2	1	3	1.5	1.5
									2

Cured under optimum conditions determined from tensile strength results.

¹ Riesl
² Stöck
³ Lüp
⁴ Bulg
⁵ Alek

⁶ Jones
⁷ Alek

⁸ Moy
⁹ Deby
¹⁰ Tim
¹¹ Scot
¹² Con

Measurement of the extraneous energy losses.—It was mentioned in Part I of this paper that during measurements on the Lüpke pendulum energy losses due to windage and vibrations were ignored as it was considered that these were small; measurements on the compound pendulum, which must possess losses of this type to a greater degree, enable the total energy absorbed during indentation to be computed, and confirm the validity of this assumption. The energy which the pendulum possesses at impact is given by the area under the force-indentation curve during indentation; this area was measured in some twenty different cases. The mean of these measurements gave an energy which was exactly equal to the potential energy which the pendulum possessed by virtue of its position prior to its release; further, and the coefficient of variation of the measurements was less than 1.5 per cent. It is felt that with more refined methods of measurement and integration this coefficient of variation will be reduced; meanwhile these results confirm that the extraneous energy losses are sufficiently small to be neglected, even with the compound pendulum.

Conclusion.—The work described in Part II of this paper is only the commencement of the measurement and analysis of the behavior of rubber during impact, but it indicates the possibilities of the use of electronic devices and the very powerful nature of the particular technique employed. A piezoelectric device such as the one discussed is capable of giving an almost complete description of the macroscopic physical behavior of the rubber during impact; it is only by a thorough investigation of complex physical properties, such as resilience, that a fuller understanding of their significance can be obtained, and apparatus and analysis similar to the one described could find many valuable applications in the field of impact testing.

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EXPOSURE CRACKING OF RUBBER *

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Exposure cracking, sometimes referred to as sun-checking or weather checking, is a term used to describe the behavior of stretched rubber when exposed to the atmosphere under conditions which cause cracking. Cracking can occur when a rubber product under slight tension is exposed to the atmosphere or to ozone. It can occur whether the product is at rest or in motion, in sunlight or in the shade; or whether the exposure is in the daytime or at night. Susceptibility to cracking may be different under these different conditions.

In a recent very excellent and comprehensive paper by Newton¹, many known facts about weathering and cracking were assembled, and the theory was proposed that all cracking of stretched rubber under exposure is due to ozone. A careful distinction was drawn between this and the crazing or weathering which occurs on unstretched rubber. If, as he contends, ozone is the active agent, the term "sun cracking" is obviously incorrect, and the term "exposure cracking" is to be preferred in describing the behavior of stretched rubber when exposed to atmospheric conditions or ozone.

In spite of the fact that we now consider all cracking of this type to be due to ozone, the testing of compounds for resistance to cracking is not a simple matter. The more obvious laboratory test methods disagree frequently with each other and with service behavior. It is difficult offhand to explain why a stock containing wax, which is excellent under static exposure of test strips, may be very bad as a tire sidewall; why an inflated tire stored in the shade may crack worse than a similar tire stored in the sun; why a tire on a parked car may crack worse than a running tire; or why a good compound in resisting sun exposure may appear to be inferior in resisting ozone.

The present work adds further weight to the new well-established ozone theory. It demonstrates clearly, however, that neither outdoor nor indoor testing is a simple matter. This work also offers for consideration new testing methods and some explanation of their meaning.

OUTDOOR TESTS

To avoid the fallacy of testing compounds under static conditions and then using them under conditions of motion, a slow-speed flexing machine was developed (Figure 1) which made possible the stretching and retraction of rubber samples in sunlight.

It should be clearly understood that this is not a fatigue test in any sense of the word. Many weather-resisting compounds contain waxes and other ingredients in excess of their solubilities, which migrate to the surface to form a film. Under dynamic conditions this film is broken purely by the relative motion of adjacent parts of the surface. Since motion rather than energy

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should be emphasized, it is possible that kinetic would be a better term than dynamic.

The stretching action was obtained by an oscillating drum, to which was attached the moving ends of the samples. This method was chosen as the simplest and cheapest way to stretch a long bank of test-strips accurately, although it has a few obvious disadvantages. It is six feet long and will hold 57 strips in one bank. It is driven through a linkage at 60 cycles per minute, and suitable adjustments have been provided to allow a minimum jaw separation of 4.5 inches, a maximum of about 9 inches, and an oscillating motion of anywhere between 0.75 inch and 1.5 inches. Further leeway in the amount of stretching can be gained by altering the taper or length of the test-piece (see below). The machine is placed facing due south, and the angle of the frame with the horizontal is about 45 degrees.



FIG. 1.—Machine for determining exposure cracking under dynamic conditions.

The test-piece is cut from a tensile sheet 2 mm. thick, and is tapered to give a uniformly varying stretch throughout its length. It is 6.5 inches overall, and at points 5 inches apart, it has widths of 0.5 inch and 1 inch, respectively. When the 5-inch portion is stretched to 5.75 inches, making an overall stretch of 15 per cent, the stretch at the large end is 10 per cent and at the small end is 22 per cent. This is basically the same idea as was used by Van Rossem², except that the variation is in width rather than in thickness, and, as a result, the strips are easily cut from the usual tensile sheet. The use of this test-piece, therefore, makes possible the simultaneous exposure of samples held statically at elongations between 10 and 22 per cent, and of samples stretched repeatedly from 0 to between 10 and 22 per cent.

TEST PROCEDURES

(1) *Static Sun Exposure.*—Sheets approximately 2 mm. thick are cured in clean steel molds which have recently been limestone blasted. No mold lubricant is used. Tapered pieces, as described above, are cut and mounted on

boards with a 5-inch section stretched to 5.75 inches. The boards are so constructed that the samples are raised 0.25 inch above their surface to allow free circulation of air. They are mounted facing due south and at an angle of about 45 degrees with the horizontal. Observations are made frequently as to both the degree and position of cracking.

(2) *Dynamic Sun Exposure.*—The preparation of the sample is the same as in the method above. The tapered pieces are mounted on the machine so adjusted that the 5-inch marked length is stretched from 5 to 5.75 inches. To minimize failures in the grips, it is the practice to run the machine only 10 hours a day: from 7:00 a.m. to 5:00 p.m.

TYPICAL RESULTS

Seven compounds were studied, all of which were typical natural-rubber white sidewall compounds. The variations were as follows:

- Compound 1 Base formula A. No wax.
- 2 Compound 1 plus 2 paraffin per 100 rubber.
- 3 Compound 1 plus 3 Sunproof per 100 rubber.
- 4 Base formula B. No wax.
- 5 Compound 4 plus 2 paraffin per 100 rubber.
- 6 Compound 4 plus 3 Sunproof per 100 rubber.
- 7 Base formula C plus 3 Sunproof per 100 rubber.

Static sun exposure under rather mild conditions (Figure 2) indicated the superiority of the wax stocks. None of the Sunproof stocks checked. The

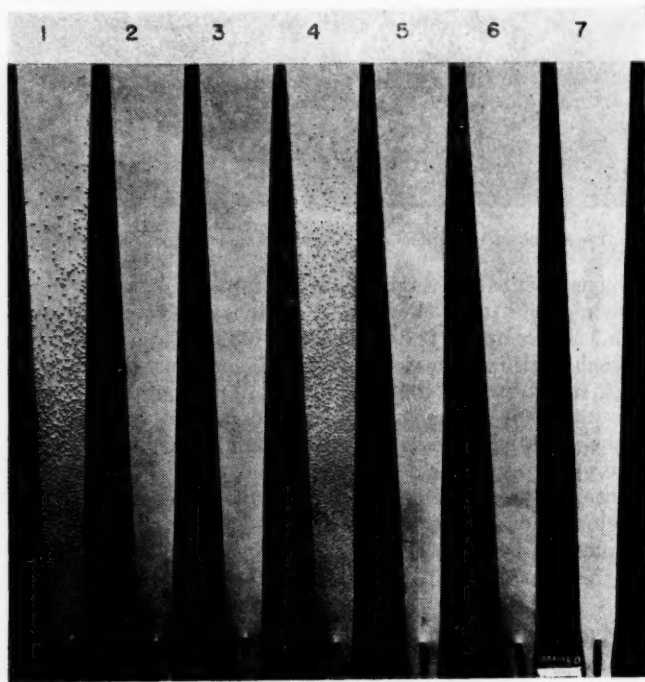


FIG. 2.—Static sun exposure; seven compounds exposed to Arizona sun for 32 days beginning December 21, 1945.

nonwax stocks were moderately checked for three-quarters of their length on the exposed side and had fine checking for their full length on the underside. The paraffin stocks showed only a little checking near the small (high elongation) end on the exposed side alone.

Dynamic checking presents a totally different picture (Figure 3). Both nonwax stocks were better than the corresponding Sunproof stocks. The paraffin stocks were nearly as bad as the Sunproof stocks. Checking on the underside was in all cases deeper and over a greater range of elongation than on the exposed side. With either type of wax, it is possible to improve resistance to dynamic cracking by suitable modification, since base formulas B and

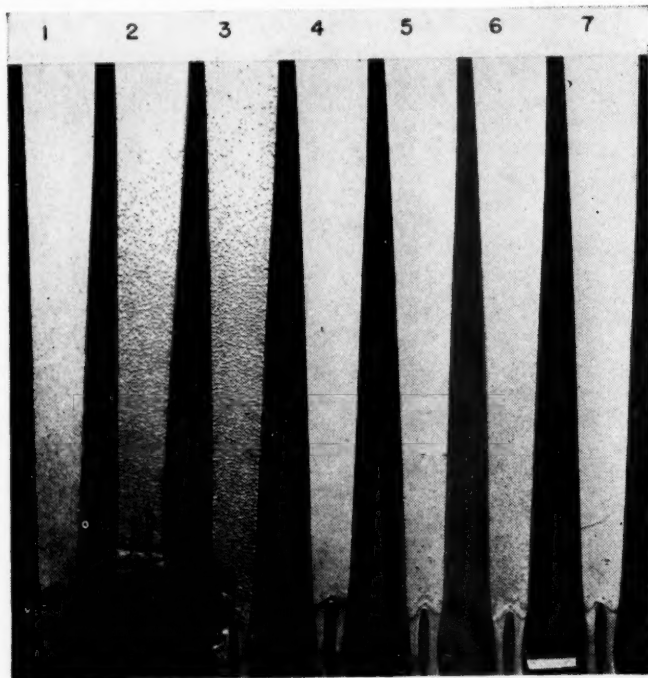


FIG. 3.—Dynamic sun exposure; seven compounds exposed to Arizona sun for seven days, beginning December 21, 1945.

C containing wax were better than base formula A containing wax. Dynamic exposure, therefore, brings out a possible danger in the use of wax and demonstrates that the danger can be at least partly overcome.

Without attempting to correlate this information too closely with tire service, it might be pointed out that the differences in the results of the two tests are certainly suggestive of some of the anomalies encountered in service.

ACCELERATED INDOOR TESTS

A brief survey of a few of the obvious indoor tests was made on this same series of compounds for the dual purpose of getting quicker methods and of throwing further light on the observed discrepancies.

Exposure to a carbon arc and a mercury arc were both considered unsatisfactory, since the one effect common to both was a hardening and degradation

of the surface without cracking in the case of the carbon arc and with cracking in the case of the mercury arc. Since the latter effect is due to the ozone produced by the mercury arc, it seemed of most interest to look into the effect of ozone in the absence of light.

For the production of ozone, U. S. air ozonizer was used, having the name plate data, Type A, 110V, 60 cycle, a single phase, one ampere. Air from a 100 lbs per sq. in. line was throttled down to a constant pressure of eight inches of water and then divided into two streams, one through $\frac{1}{4}$ -inch tubing and one through a small capillary. The latter was passed, without drying, through the ozonizer and thence to a vented chamber, and was introduced at such an angle that it produced turbulence and diluted the stream of ozone before either

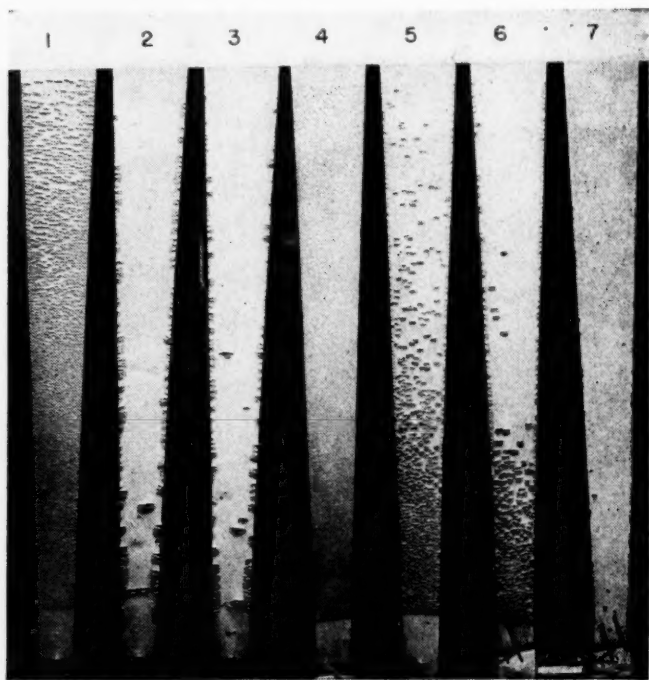


FIG. 4.—Immediate ozone exposure; seven compounds exposed to ozone for 30 minutes; no preconditioning of samples.

stream could reach the samples. The result accomplished was an unknown, but fairly constant and reproducible concentration of ozone. It was such that its odor seemed quite strong and that it produced the first very slight checks in Compound 1 in four minutes and rather severe checking in 30 minutes.

Samples of the same seven compounds were prepared and stretched as in method (1) and were put into the ozone chamber two hours after stretching. Results after 30 minutes are shown in Figure 4. There are differences between the compounds in degree and type of checking, and the results are very much like those of the mercury-arc exposure. The nonwax stocks showed single straight checks and seemed to check to all elongations. The wax stocks showed fewer and deeper checks, which usually occurred in groups consisting of two large parallel cracks with several small ones between them.

The fact that the wax compounds had fewer but deeper checks leads to the conclusion that a wax film on the surface must offer some protection against ozone, but that once the ozone has started to penetrate, this protection is lost.

PRECONDITIONING FOR OZONE TEST

Various methods of preconditioning were attempted on Compound 6 as follows:

- (A) Stretch. Age three days at room temperature. Expose.
- (B) Stretch. Acetone wash. Age three days at room temperature. Expose.
- (C) Stretch. Expose immediately.
- (D) Acetone wash. Age three days at room temperature. Expose.
- (E) Stretch. Acetone wash. Expose immediately.
- (F) Stretch. Heat 10 minutes at 100° C. Age three days at room temperature. Expose.

The differences after 30 minutes' exposure were quite striking (Figure 5). The sample stretched and exposed immediately had large deep cracks for its

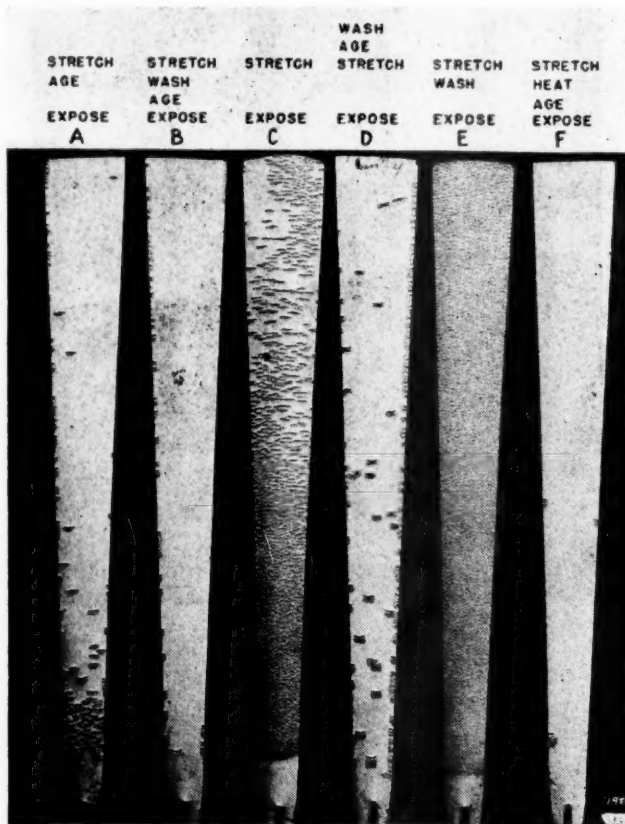


Fig. 5.—Preconditioning for ozone; compound 6 treated as indicated and exposed to ozone for 30 minutes.

full length. The methods tending to give the most uniform wax films: namely, (A), (B), and (F), had the fewest checks and the largest unchecked areas. Most interesting of all, the sample which was washed to remove the wax film and then exposed before a new film could bloom out (E), had all the appearance of a nonwax stock. Checking was uniform, fine grained, and covered the full length of the strip.

This is conclusive evidence that, for proper interpretation of an ozone test, it is imperative to control the surface condition of the sample. With this point in mind, two procedures were set up: one which should favor the formation of unbroken films on the surface, and one which should remove the films entirely.

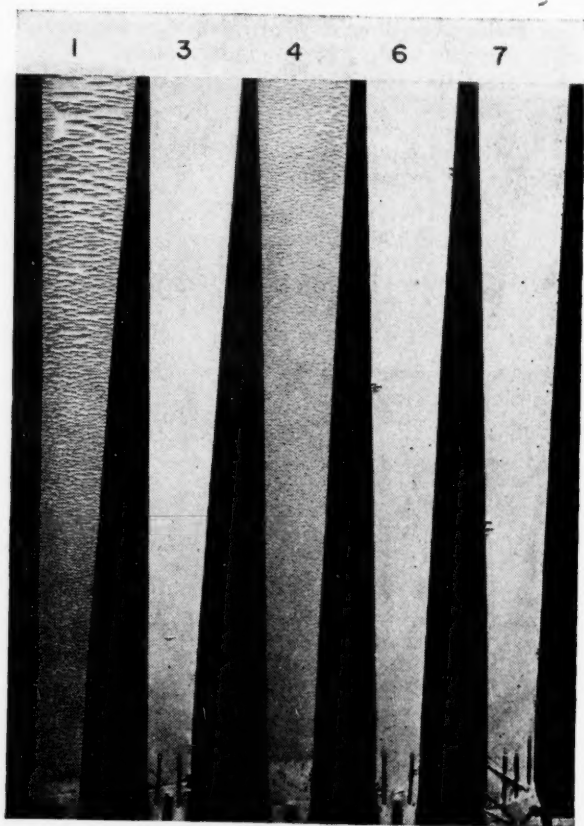


FIG. 6.—Ozone exposure—unbroken films; five compounds stretched, heated, and aged three days before exposing for 30 minutes.

TEST PROCEDURES

(3) *Ozone Unbroken Films.*—Samples are prepared and stretched as in method (1). After stretching, they are heated 10 minutes at 100° C to melt or dissolve the wax film. They are then aged three days at room temperature in the stretched position to allow a new film to form, and are then exposed to diluted ozone for 30 minutes.

(4) *Ozone Films Removed*.—Samples are prepared as in method (1). They are then thoroughly washed with acetone and stretched while still wet. They are washed again and put into diluted ozone when dry (in about five minutes). Exposure is 30 minutes.

TYPICAL RESULTS

Five of the compounds previously used were tested by these methods. With method (3), having supposedly unbroken films, the nonwax compounds, 1 and 4, checked quite uniformly for their full length (Figure 6). The three wax compounds, 3, 6, and 7, did not check for the greater part of 30 minutes. Near the end of this period a few isolated checks appeared and, once they had appeared, grew very rapidly. The most vulnerable part of the strip was apparently near the edges where the wax film should be thinnest and where ozone could diffuse both through the edges and through the flat surface. Once sufficient ozone had penetrated to start a crack, the wax film was broken, and then the cracking proceeded rapidly.

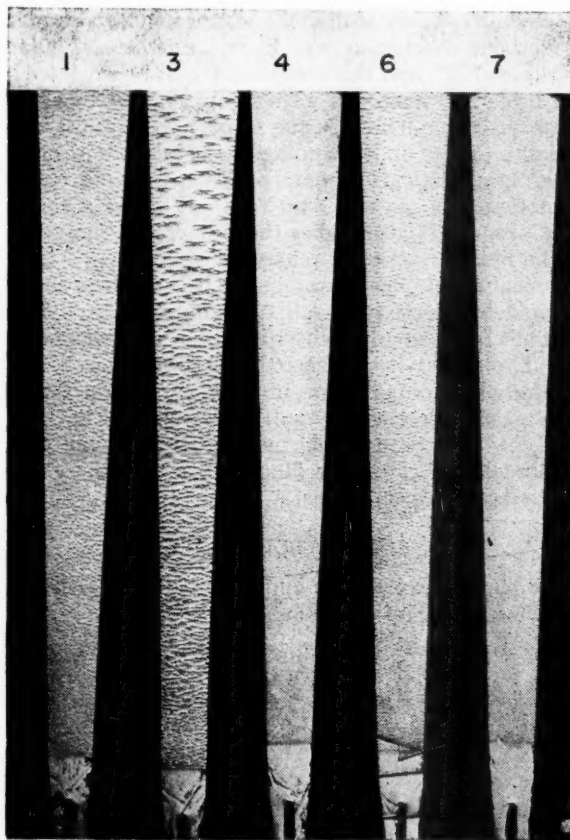


FIG. 7.—Ozone exposure—films removed; five compounds washed thoroughly with acetone, stretched, washed again, and exposed for 30 minutes as soon as dry.

The same compounds were tested by method (4) with the films removed. All samples had the appearance of nonwax stocks in that checking was fairly uniform for the full length. It was a surprise to find that the wax stocks 3 and 6 were poorer than the nonwax stocks 1 and 4, respectively. The modified formula at least partly overcame this undesirable effect of wax (Figure 7).

This phase of the work leads to the very important conclusion that wax plays a dual role. It protects against ozone by forming a film, and it also makes the stock more vulnerable to ozone if the film is broken or removed. Again it may be pointed out that this effect is suggestive of some of the discrepancies between roof aging and tire service.

DISCUSSION

Two distinct conditions of outdoor sun cracking have been demonstrated: (1) the old static method and (2) a newer dynamic method. It is felt that the real distinction between these is brought about, not by any fatigue of the rubber, but rather by the breaking of wax films.

Two distinct conditions of laboratory ozone cracking have been demonstrated (3) with continuous wax films and (4) with wax films removed. The results of (3) are similar to those of (1), and this similarity would be expected since in both methods continuous wax films are favored. The results of (4) are parallel to those of (2), and this condition might be expected, since the wax films are either broken or removed. This point is consistent with the current theory that all exposure cracking is due to ozone. It illustrates particularly the importance of a proper understanding of the laboratory methods.

By applying these methods to compounds containing common waxes, it has been shown that wax plays a dual role. It forms a surface film which protects against ozone. It also makes the rubber internally more vulnerable to ozone once the film is cracked or removed.

From a practical development standpoint it is obvious that none of these test methods could be adequate for all types of work. Obviously a piece of rubber that will not be flexed in service should not be developed by means of a dynamic test. The service conditions that a tire sidewall must meet vary probably over the whole range from purely static exposure to severe flexing. If a car is driven only occasionally and is then parked outside, it is not far removed from dynamic exposure, and more reliance should be placed on the methods which break or remove the films. Of course the ideal compound is the best under both sets of conditions.

ACKNOWLEDGMENT

The author wishes to express his appreciation to F. J. Dugan, chief compounder of the Goodyear Tire & Rubber Co.

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THE RHEOLOGY OF PROCESSING QUALITY OF RAW RUBBERS *

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INTRODUCTION

After a crude rubber, such as Hevea or GR-S, has been compounded with the ingredients necessary for vulcanizing, or curing, the raw mix must be formed in some way before it is cured. This forming operation is nearly always either calendering or extruding. Naturally, it is important that the stock should take the desired form as closely as possible; but in practice it is found that elastomers are in general difficult to form. It seems to be inevitable that those materials which exhibit long-range elasticity after curing also exhibit considerable elasticity before curing and refuse, therefore, to hold their shape after a forming operation.

This and other processing troubles were handled in the early history of the rubber industry simply by trial-and-error methods in the factories. Later, particularly during the last ten years, further progress in processing problems was made by introducing various plastometers and other devices for testing specific properties of the raw stock. These test methods replaced simple tests by hand and by visual inspection, and made it possible to set up specifications for some of the stock properties empirically found necessary for acceptable processing.

As a final step in processing control, there are now being developed, in the industry, methods for making quantitative measurements of particular processing defects. Such methods involve a small or full-scale processing operation under standardized conditions, and a standardized procedure for quantitative evaluation of the results in terms of departures from perfection.

In the present discussion of processing quality of raw stocks in the rubber industry, various specific processing defects are described, various rheological methods used for testing raw stocks are mentioned, and finally, a few experimental results are reported which show correlations between some of the rheological tests and quantitative measurements of certain processing properties.

PROCESSING DEFECTS

The most striking, and perhaps the most troublesome, defect is caused by elastic recovery, which produces a shrinkage in the length of the extruded or calendered material, accompanied by an increase in thickness and width. As suggested above, this defect is apparently an essential characteristic of any material showing long-range elasticity in its final or cured state. Consequently, all that the rubber technologist can hope to do is to limit the recovery as much as possible without damage to the quality of the finished product, and he must allow for some shrinkage in all cases.

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If shrinkage is not uniform throughout the mass of the formed stock, surface irregularities necessarily develop. If the stock is subsequently cured in a mold, moderate roughness of the surface in the raw state is of no consequence. On the other hand, if the material is to be cured in open steam, as is the practice, for example, in manufacturing rubber footwear, surface irregularities constitute a serious defect. Furthermore, a stock which calenders rough where it should be smooth also develops blemishes in any pattern embossed in the sheet.

Aside from irregularities in elastic recovery, there are other possible sources of surface roughness. One of these, encountered in calendering operations, arises apparently from the failure of the stock to form completely as it passes between the calender rolls. The calendered stock then has small valleys or pockets scattered over the surface. A defect encountered in extruding operations consists of saw-toothed tears in the surface. These develop as a result of friction of the stock against the extruder die, especially at any narrow peripheral section where the flow is retarded and the faster moving stock in the center pulls on the slower edges.

Occasionally, a compounded stock is encountered which fails to pass through an extruder, or goes so slowly as to result in incipient curing, or scorching of the stock. Surface roughness then develops because of broken lumps of the scorched stock, or the extruder may be stopped up completely. Scorching frequently occurs in a stock which extrudes at a normal speed but which overheats because of its high viscosity.

RHEOLOGICAL TESTS

Before attempting to analyze in rheological terms the various properties of the stock which lead to the above processing defects, we shall discuss briefly the various rheological measurements which have been developed in the rubber industry. Of these, the one most frequently used is a viscosity measurement. Tests of this type are generally referred to in the industry as plasticity tests, but in many cases this term is a misnomer, since the measurement as usually made yields only a stress-rate of strain relationship under some particular set of test conditions. Any relationship between such a single viscosity figure and true plasticity, in any reasonable sense of the latter word, is purely coincidental.

The earliest and simplest instrument for measuring the viscosity of rubbers is the Williams plastometer¹, which consists essentially of a 5-kg. weight which rests on and compresses the sample, initially in the form of a pellet or short cylinder. The figure usually reported in the test is the thickness of the sample after three minutes' compression at a standard temperature. Theoretical formulas² have been developed for calculating viscosity from such measurements. If applied to rubbers, none of these formulas can be accepted as accurate, since they ignore the thixotropy of the material, which is pronounced in all commercial rubbers. Nevertheless, the Williams and similar instruments³ have found considerable useful application as empirical tests.

In viscometers of the extrusion type, first used extensively by Marzetti⁴, the sample, contained in a cylinder, is forced by compressed air or by a moving piston to extrude through a small orifice. The rate of extrusion under various pressures is measurable. The most elaborate but most rapid and convenient extrusion viscometer is that developed by Dillon⁵. An auxiliary preheater for the sample saves considerable time and makes it possible to attain an operating cycle of 1.5 minutes per sample. The most obvious formula for calculating viscosity from such a test is that expressed in Poiseuille's Law. However, even if the orifice consists of a tube of considerable length in comparison with

its diameter, this law cannot be applied to this test with any reliance. This is true also of a more sophisticated formula⁶ which is obtained by allowing both for departure from the Newtonian law of flow and for slippage along the surface of the capillary. The reason for the failure of such formulas to give correct values for viscosity again lies in the high thixotropy of the material. In a series of measurements of extrusion through circular dies of various diameters and lengths, it was found that the energy required to deform the sample within the cylinder and get it started into the die was from one-third to one-half of the total energy required for the extrusion. Thus, for example, the pressure required to maintain a given rate of extrusion through a $\frac{1}{8}$ inch capillary 0.6 inch long was only twice that required to maintain the same rate of extrusion through a hole of the same diameter but 0.06 inch long. Such results clearly indicate that it is unsafe to calculate viscosity from extrusion measurements which do not permit a quantitative separation of preorifice and interorifice work of extrusion. These remarks of course do not question the value of an extrusion plastometer as an empirical factory control instrument.

A third type of rubber viscometer subjects the sample to a continuous shearing deformation. Such instruments have been developed in two forms, the first being a rotating cylinder viscometer⁷ particularly adapted to the measuring of true viscosity as well as elastic recovery, the second one being a rotating disk viscometer⁸ with a single speed of rotation and designed particularly for factory control work. In both instruments the metal parts in contact with the sample are fluted or cross-hatched to prevent slipping. In the first instrument, which we may call a rubber rheometer, the precision attainable is somewhat reduced by the friction of auxiliary devices required to keep the sample from working out of the space between the cylinders. Nevertheless, the precision is quite adequate for many purposes. True viscosities over a wide range of rates of shear can be reliably determined and also elastic recovery; in addition, the modulus and damping factor in free vibrations at frequencies of the order of 10 cycles per second. While this rheometer is quite effective in scientific investigations, it is much too slow for factory control work. The shearing disk viscometer, developed for the latter purpose, consists essentially of a disk rotating within a shallow, cup-shaped cavity. The torque required to maintain a given speed of rotation is measured. When multiplied by a numerical factor, the reading of the instrument is converted to an effective viscosity as averaged over a range of shearing extending from zero at the center of the rotating disk to the maximum at the periphery. The standard commercial instrument of this type operates at a single speed of 2 r.p.m.; but one experimental instrument has been fitted with a three-speed drive of 2, 4 and 8 r.p.m.

In a recent modification of the disk viscometer, developed by Piper and Scott⁹, a wide range of speeds is available; and, furthermore, the disk rotor is replaced with a conical rotor, which has the advantage that the rate of shear is essentially uniform throughout the sample, as in the cylindrical viscometer.

In addition to viscosity, the elastic recovery of a stock is frequently measured. In a compression test, this is the recovery in height of the sample after a few minutes release from the compressing load. In an extrusion test, it is the ratio of the section dimensions of the extruded stock, after recovery is complete, to the dimensions of the extruder die. In the shearing test, it is the reverse rotation of the rotor after being released from the driving mechanism. The three-speed shearing disk viscometer mentioned above has also a clutch release and indicating mechanism which make possible measurement of elastic recovery.

Tack, or the ability of raw stock to adhere to itself or to other materials, is of considerable importance in building operations, such as the assembly of the rubber and fabric parts of a tire. In spite of its importance, tack has usually been estimated only by crude hand tests; but apparatus and methods for quantitative measurements have recently been described¹⁰. Such measurements, aside from their direct application to building operations, can probably be of considerable value in studying the rheology of rubbers, because tack is undoubtedly closely related to the ability of the molecules within a rubber sample to form quickly new attachments of full strength when, in the continuous deformation of the sample, they are forced into new configurations. Thus, we should expect high tack to be correlated with low thixotropy, thixotropy being dependent on the difference in the strength of an old in comparison with a newly established intermolecular attachment.

Another property of rubbers of practical importance, and perhaps related to tack, is friction against hot metal. In the process of extrusion, the rubber must move over the metal surfaces of the extrusion barrel, the screw, and the die. If the friction is too high, slippage of the rubber over the metal is retarded, and those processing troubles associated with slow extrusion, referred to above, develop. Nevertheless, in spite of the importance of friction of raw rubber on hot metal, there is no published method for measuring it. Various attempts made by the present writer to develop such a method have been unsuccessful. In the extrusion experiments referred to above, the slip velocity was too small in comparison with the mean velocity of the extrusion to be measurable with the apparatus employed. A more critical test, employing the shearing disk plastometer, likewise indicated a zero velocity of slip within the precision of the measurements. In this test a special rotor with a smooth surface was compared with a standard rotor with a knurled surface, the theory being that the rubber would slip on the surface of the smooth rotor and yield a lower reading with a given stock. The very surprising results were that the smooth rotor gave slightly higher readings. The smooth rotor had the same dimensions as the outside of the knurled rotor; and apparently any slippage that took place on the smoother rotor was so small that it was not sufficient even to compensate for the slight difference in mean dimensions of the two rotors.

The discussion of all the above measurements has been on the tacit assumption that the material in the test was homogeneous. This assumption, of course, cannot be strictly valid and, as a matter of fact, there is good reason to suspect that some processing defects, particularly roughness, are partly due to inhomogeneity. Aside from incomplete mixing of compounding ingredients, one possible source of inhomogeneity lies in nonuniformity of the rubber itself. Such lack of uniformity could result from incomplete and nonuniform breakdown of the crude rubber or from local variations in the degree or type of polymerization in synthetic rubbers. It would seem, therefore, that some direct measurement of nonuniformity of viscosity or hardness in a raw mixed stock would be useful, but, so far as the writer knows, no one has yet attempted to develop such a measurement.

CORRELATION BETWEEN RHEOLOGICAL TESTS AND PROCESSING PROPERTIES

We shall now consider the extent to which the above rheological measurements can be used to predict processing quality. The ideal situation would be one in which quantitative tests were available for all processing defects, and

the values obtained in such measurements on any particular stock could be predicted from a proper selection of rheological measurements made on the stock before processing. We are far from reaching this goal, but at least some progress can be reported.

The most obvious and direct application of a viscosity measurement would be in predicting the power consumption in the calender or extruder. Such a check with regard to calendering has not yet been made, to the author's knowledge; but, in extruding operations, it has been found by Vila¹¹ that the power consumed increases linearly with the mean viscosity, as measured with the shearing disk viscometer. The power consumption is usually not of primary importance in itself, but, since the power is mostly converted into heat in the rubber, the high power necessarily consumed in a stock of high viscosity results in scorching.

Another processing property obviously and closely related to a simple rheological measurement is shrinkage. Calender shrinkage is the lengthwise shrinkage of a calendered sheet compared with the length of the sheet while on the calender roll. Shrinkage may be permitted to take place while the sample is immersed or floating in hot water or while it is resting on a table top dusted with talc. Figure 1 shows the correlation that was obtained in one experiment

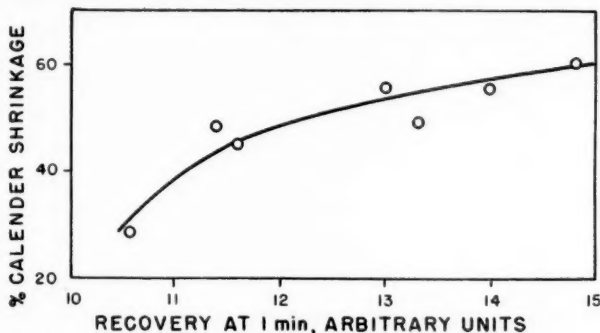


FIG. 1.—Calender shrinkage vs. elastic recovery in the disk viscometer

between calender shrinkage of a group of commercial stocks and the elastic recovery as measured in the disk viscometer. The correlation in this case is fairly good. On the other hand, in several other calendering programs carried out by L. M. White of the General Laboratories of the U. S. Rubber Company, involving a narrower range in type of stock, no correlation was found between shrinkage and measured elastic recovery¹². The data showed definitely that the trouble could not be attributed simply to experimental error. It may be pointed out that in the calendering operation the stock before shrinkage is subjected to a momentary, very high rate of deformation in passing through the nip, followed by a period of fixed strain while on the calender roll. If the viscometer rotor could be given a momentary high rate of rotation, the subsequent elastic recovery might be found to correlate better with calender shrinkage.

Shrinkage after an extruding operation has been measured by Zapp and Gessler¹³ and compared with rheological measurements obtained with a compression type of instrument. The rheological function found to give good correlation with shrinkage, or lateral swell, was R/P , where P , the "plasticity", is the load required to compress the test cylinder to half its original height in

10 seconds, and R is the subsequent percentage elastic recovery. The stocks tested were Butyl rubbers of different molecular weights and molecular-weight distributions, all compounded with 50 parts of channel black. Figure 2 shows the correlation obtained, which is good except for one point badly off.

Some efforts made by the author to correlate recovery with the extruder shrinkage failed completely, and the correlation could not be improved by combining recovery with viscosity data, as was done by Zapp and Gessler. Apparently shrinkage after calendaring or extruding is a more complex phenomenon than might be assumed, and more work will be required before it can be well understood.

Mention has been made of the fact that stocks are sometimes encountered which give trouble in the factory because of low rates of extrusion. So far as simple, or Newtonian, viscosity is concerned, there is no reason to anticipate that the rate of extrusion would be reduced by high viscosity. Velocity of rotation of the screw can usually be maintained in spite of the increased powder

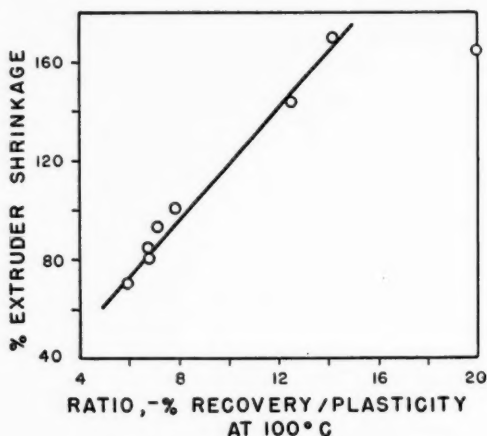


FIG. 2.—Extruder shrinkage vs. recovery/plasticity, on series of Butyl rubber stocks of different mol. wts., 100 parts by weight, compounded with 50 parts easy processing channel black. From Zapp and Gessler.

consumption, and, while high viscosity necessarily increases the pressure required to push the stock through the die, the stresses developed within the stock by the forced movements within the barrel would also be increased, and presumably in the same proportion. Obviously, to find any solution to the problem of rate of extrusion, we must cease thinking in terms of simple viscosity and consider the rheological diagram, or the stress-rate of shear relationship over the rates of shear developed in the extrusion process. With this idea in mind, the rates of extrusion of some experimental stocks in a No. $\frac{1}{2}$ Royle extruder were compared with a measure of the relative increase in viscosity reading with rate of shear obtained with the three-speed shearing disk viscometer. Only the two extreme speeds, 2 and 8 r.p.m., were employed; and the function calculated for comparison with rate of extrusion was the relative stress increment:

$$I_s = \frac{V_8 - V_2}{V_2},$$

in which V_2 and V_8 are, respectively, the shearing disk readings at 2 and 8 r.p.m. The temperature of the viscometer was adjusted to the observed temperature of the stocks as they came out of the extruder.

The degree of correlation found is shown in Fig. 3. In connection with this figure, it should be mentioned that four of the stocks, in pairs, were the same except for the addition of a commercial softener—pine tar in one case, stearic acid in the other. These softeners are generally considered to have a lubricating effect, which reduces the friction of the stocks on the interior extruder surfaces. While such an effect on ease of slippage may possibly occur, the data show that the stress increment also is increased by the softeners. The correlation shown in Fig. 3, therefore, suggests strongly that in this connection it is the effect of the stress increment which is of major importance. The stocks represented by the data were of a wide variety, involving hard and soft carbon blacks, gum stocks, and some commercial stocks of high shrinkage and low shrinkage, and it is very unlikely that the close correlation shown would have been obtained unless the stress increment were the primary factor determining rate of extrusion.

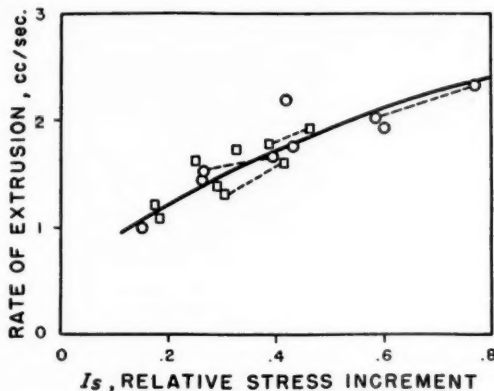


FIG. 3.—Rate of extrusion vs. relative stress increment, $(V_8 - V_2)/V_2$, where V_8 and V_2 are the disk viscosity readings at 8 and 2 r.p.m., respectively. Points connected by dotted lines are similar stocks with and without softener, the one with softener having the larger I_s in all cases. Circles indicate a circular die; squares indicate a rectangular die.

The fact that the rate of extrusion increases with the stress increment can be understood if we assume that in the barrel, where the extruding pressure is developed, the effective rate of shear is higher than in the throat and die, where the opposing force is developed.

The defect of surface roughness results undoubtedly in a very complex way from a considerable number of different rheological properties. While roughness can be and has been approximately rated by visual inspection, such a method is obviously inadequate for any precise analysis of the problem. A recently developed apparatus for measuring the roughness of calendered sheet, called a rugosimeter, has been described in the literature¹⁴. The test depends essentially on the resistance to air flow between the rough surface of the sample and a circular test-plate resting on it. The rougher the surface, the lower the resistance to flow. On the assumption that the surface irregularities are sinusoidal in profile, the flow resistance can be converted to the mean effective height of the irregularities. This effective height is called the rugosity.

The stock properties of conceivable importance in rugosity would include elastic recovery, inhomogeneity, thixotropy, tack, and the rheological diagram of stress-rate of strain curve.

Elastic recovery produces roughness if the recovery is not uniform. Inhomogeneity of the stock causes nonuniformity in recovery. The same effect results also from thixotropy, for in this case local variations in immediate past history of shearing action within the rolling bank cause temporary, local variations in viscosity. Variations in viscosity, or local hard spots, may also cause failure of the sheet to form completely, aside from irregularity in elastic recovery. Low tack probably means high thixotropy and, hence, rough calendering. Low tack probably has also a direct effect in causing pockets, because of failure of rubber surfaces to adhere even when forced into contact within the bite. Large curvature in the rheological diagram, or large departure from Newtonian viscosity, probably means high thixotropy and, hence, rough calendering. The shape of the rheological diagram probably influences also the perfection of forming within the bite, but the precise nature of this influence is not easily predicted.

This discussion indicates what sort of rheological measurements we may expect to find correlated with rugosity measurements. It indicates also, however, that some of the rheological properties mentioned are interrelated. Hence, to find close multiple correlation between rugosity and the rheological properties, it may be necessary to include all of the rheological properties that have been mentioned.

Figure 4 shows the correlation found in one experiment between rugosity and certain rheological properties. This experiment was made before the rugosimeter was developed to its present stage, but the fundamental principle of the roughness measurement was, nevertheless, the same. As is evident from

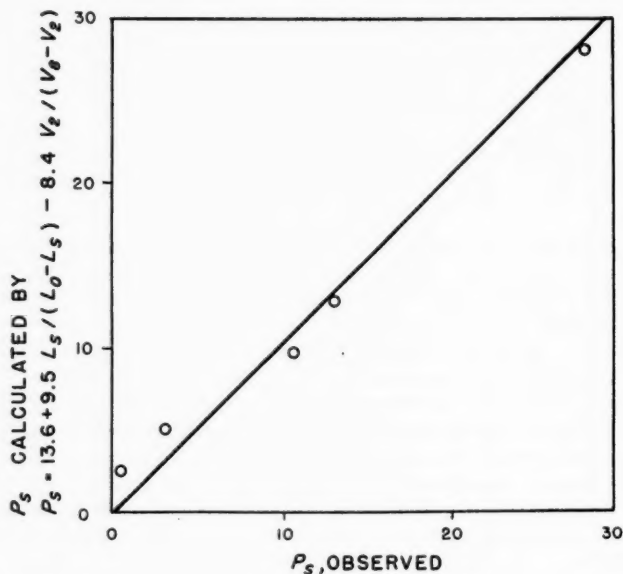


Fig. 4.—Calculated and observed P_s . P_s is a measure of smoothness. $L_s/(L_0 - L_s)$ is calender shrinkage. V_1 and V_2 are the disk viscosity readings at 8 and 2 r.p.m.

the figure, the range in roughness exhibited by the selected stocks is wide. The rheological function found to correlate with rugosity, or, in this case, an inverse measure of rugosity, or smoothness, is indicated by the equation:

$$P_s = 13.6 + 9.50 \frac{L_s}{L_0 - L_s} - 8.40 \frac{V_2}{V_8 - V_2}$$

where P_s is the smoothness, $(L_0 - L_s)/L_s$ is the percentage calender shrinkage, and V_2 and V_8 are the viscosity readings at 2 and 8 r.p.m., respectively, as previously defined. For the first rheological factor in the equation, elastic recovery would be preferred, but the accessory of the disk viscometer for measuring elastic recovery had not at this time been satisfactorily developed. Consequently, instead of elastic recovery, shrinkage as measured on the calendered sheet was used. The second factor is the reciprocal of the relative stress increment previously defined. According to generally accepted ideas, the larger the stress increment, the lower is the "structure viscosity" and likewise the thixotropy of the material.

This equation tells us that the smoothness of the calendered sheet increases as the shrinkage decreases and as the stress increment increases. This was to be expected on the basis of the preceding discussion of the effects of thixotropy and nonuniform elastic recovery.

A later attempt to repeat these results with another group of stocks was not successful when the same rheological function was tried; but fair correlation with roughness was obtained by including an additional factor in the rheological function. This factor was the ratio of the breaking tensile force to the force at 100 per cent elongation in a dumbbell test-piece of the raw stock when pulled at a temperature of 70° C. This ratio may conceivably be a measure of the ratio of highest to the average elastic stress within the rubber as it comes through the calender rolls.

A different approach to the problem of processing quality has led to the development, by Garvey, Whitlock, and Freese¹⁵, of a special small-scale extrusion test. The die used has an orifice which is essentially trapezoidal in form, with a sharp angle of approximately 20° at one corner. The processing quality of a stock is taken as the average of visual ratings for the four properties, (1) section contour of the extruded stock, (2) tearing at the sharp corner, (3) surface roughness, (4) corner sharpness. The test is reported to be reliable in predicting processing behavior in large-scale extruders. It has the obvious disadvantage of depending on visual ratings, but it would probably be possible to develop instrumental measurements for at least some of these ratings.

With regard to the way in which the four ratings obtained in this test are used together in an arbitrary averaging procedure, it can only be stated that, from either a scientific or a practical point of view, such a procedure is, in this writer's opinion, to be deplored. Since we recognize and have independent measurements of different processing defects, we should cease thinking of processing quality as a single, one-dimensional property.

From the various experimental results that have been reviewed here, it is obvious that our present understanding of the rheology of processing quality is very incomplete, but that a substantial beginning has been made. Doubtless, our limited understanding will improve as more and better tests are developed and more attempts are made to establish empirical relationships between rheological properties and measurable processing qualities. Eventually, on the basis of such empirical knowledge theoretical treatments of calendering and extruding quality will doubtless be developed.

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PROPERTIES OF HARD RUBBER. XXI. INFLUENCE OF VULCANIZATION TEMPERATURE *

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GENERAL PLAN OF THE INVESTIGATION

This report, a continuation of the joint investigation with the British Electrical and Allied Industries Research Association of the properties of unloaded hard rubber as affected by composition and method of manufacture, deals particularly with the influence of vulcanization temperature. It is well known, of course, that temperature has a great influence on the rate of vulcanization or combination of sulfur; but the main object of this work was to ascertain the effect of this factor on the properties of the product after making allowance for differences in rate of vulcanization.

The object of the previous stage of the investigation¹ was to ascertain the best rubber-sulfur ratio and time of vulcanization at a fixed vulcanizing temperature of 155° C, and it was intended to adopt this composition and vulcanize at three different temperatures for periods equivalent at each temperature to the optimum period at 155° C. Although the results pointed generally to an optimum of 5 hours at 155° C, they were not decisive as to a single rubber-sulfur ratio being best for all purposes. However, it was considered that sufficient information would be obtained in the present investigation by testing two rubber-sulfur mixings, 65/35 and 70/30, vulcanized for one period at each of three temperatures, 165°, 155°, and 135° C.

To ensure that the vulcanization periods adopted at the different temperatures were equivalent to one another, smaller quantities of the materials were vulcanized for shorter and longer periods, and tested for plastic flow and percentage of free sulfur.

Stocks were mixed from the same averaged rubber and sulfur as before¹ and vulcanized by the same method, *i.e.*, by a preliminary molding in a daylight press, followed by a final molding in an autoclave press, in each case after a uniform temperature rise.

The following properties were tested by the same methods as before¹: percentage of free sulfur, density, cross-breaking strength and deflection, impact strength (notched and unnotched), plastic yield and yield temperature, permissibility and power factor, and surface discoloration in daylight.

PREPARATION OF SAMPLES

The stocks, F and G, of rubber-sulfur ratio 65/35 and 70/30, respectively, were mixed in the same way, and from the same averaged rubber and sulfur as in Part I (a). Four sheets, 25 cm. square and 5 mm. (3/16 inch) thick, of

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each mixing were vulcanized at each of the three temperatures, 165°, 155°, and 135° C, corresponding to 86, 64, and 31 lb. per sq. in. steam pressure, respectively. The method of vulcanization was the same as before, namely, a preliminary molding in the daylight press for a period equivalent to 50 minutes at 155° C, during which shrinkage took place, followed by a final molding in thinner molds in the autoclave press, after a uniform temperature rise of about 55° C per hour from 100° C per hour from 100° C in each case. At the lower temperatures continuous vulcanization was not possible, since it extended over several working days, so a similar rise was given at each reheating. The actual times at vulcanizing temperature and the number of rises are shown in Table 1.

TABLE 1
TIME AT VULCANIZING TEMPERATURE AND NUMBER OF RISES

135° C			155° C			165° C		
Time		Rises	Time		Rises	Time		Rises
hrs.	min.		hrs.	min.		hrs.	min.	
17	20	4	3	0	2	1	4	2
21	20	4	3	45	2	1	23	2
28	0	5	5	0	2	1	56	2
56	50	10	10	30	2	4	19	2

For the purpose of determining equivalent vulcanizing times at the different temperatures, it is calculated that the rises were equivalent to the following periods at vulcanizing temperature:

Rise at 55° C per hour from

100° to 135° C = 12 min. at 135° C

100° to 155° C = 13 min. at 155° C

100° to 165° C = 13 min. at 165° C

The equivalent vulcanization times at the various temperatures were estimated by assuming a factorial temperature coefficient of 2.3 per 10° C, and allowing for the rises as above. To check the validity of this estimation, small samples of the same material were vulcanized for various shorter and longer periods as shown in Table 1 (estimated to be equivalent to 3, 3½, and 10½ hours at 155° C with two rises) and tested for plastic yield temperature and percentage of free sulfur, thus enabling vulcanization time-yield curves to be plotted.

When the impact strength results were obtained, certain anomalous figures were found, and these were at first attributed to faults in mixing. It was later suggested, however, that these might be due to the frequent interruptions necessary in carrying out long vulcanizations in daily periods. The vulcanization of certain confirmatory samples was, therefore, carried out continuously in the laboratories of the India Rubber, Gutta-Percha and Telegraph Works Co., Ltd., after preliminary molding at the R.A.B.R.M. laboratories, and these samples were tested for comparison with the first set of results. The samples repeated in this way were of both mixings, vulcanized for one period at each of the temperatures 135° and 155° C. The vulcanization conditions for these confirmatory samples were:

Vulcanization temperature	Number of rises	Time at vulcanizing temperature	
		hrs.	min.
155° C	2	5	0
135° C	2	28	0

All samples will be referred to in this report by their mixing letters F and G

and the temperature of vulcanization, *e.g.*, F/135° C signifies a sample with rubber-sulfur ratio 65/35 and vulcanized at 135° C. Unless otherwise stated, the vulcanization time is estimated to be equivalent to 5 hours at 155° C with two rises.

TEST OF EQUIVALENT VULCANIZATION TIMES

The results of plastic yield and free sulfur tests made on samples vulcanized for various periods to ensure that the conditions adopted as equivalent to 5 hours at 155° C were correct are shown in Table 2. This table includes also

TABLE 2
YIELD TEMPERATURES AND PERCENTAGES OF FREE SULFUR OF SAMPLES
VULCANIZED FOR VARIOUS PERIODS

Sample	Yield tempera- ture (° C)	Free sulfur (per cent)	Sample	Yield tempera- ture (° C)	Free sulfur (per cent)	Total equivalent vulcanization time	
						hrs.	min.
F/165° C	71	5.0	G/165° C	65	2.1	1	30
	77.5	3.9		70	1.4	1	49
	80	3.3		76.5	0.95	2	22
	79	3.0		78	0.8	4	45
F/155° C	71	4.9	G/155° C	63	2.4	3	26
	80	4.1		72	1.4	4	11
	83	3.4		78.5	0.9	5	26
	83.5	3.0		83	0.6	10	56
F/135° C	63	5.4	G/135° C	59	3.2	18	8
	78	3.9		72	1.7	22	8
	85	3.2		79	0.9	29	0
	89.5	3.0		85	0.6	58	50
A(65/35)	59.6	6.5	70/30 (estd.)	52.5	3.5	3	26
	75.5	4.9		70	1.85	4	11
	83.2	3.8		79	1.0	5	26
	84.3	3.7		81	0.9	7	26
	85.6	3.8		81	0.8	10	56

for comparison (1) the results for Mixing A (65/35) of the previous work¹, and (2) an estimated value for a 70/30 mixing by interpolation between the results for Mixings A, B, and C of the earlier work¹. The total equivalent vulcanization times include the allowance for the rise, the corrected values corresponding to a temperature coefficient of 2.3 for the rate of vulcanization.

The yield temperatures are plotted against vulcanization time in Figures 1 and 2, and the percentages of free sulfur in Figures 3 and 4. The following points of interest in connection with the correspondence of the states of vulcanization due to the various vulcanization temperatures will be noted.

1. The rates of vulcanization of F/155° C and G/155° C, as judged by yield temperature, are a little greater than those of A and 70/30 (estimated) from the previous work¹, due probably to slight differences in vulcanizing conditions, such as temperature, uniformity of rises, and the like. The difference is not very important so far as the comparison of materials vulcanized for the equivalent of 5 hours at 155° C is concerned, because these points, as intended, lie near the beginning of the flat part of the vulcanization time-yield curve where most properties are comparatively insensitive to changes in vulcanization time. The difference in rates of vulcanization is supported by the free sulfur figures.

2. It was intended from these tests to obtain a more accurate figure for the temperature coefficient of vulcanization. It is seen, however, that the yield temperature approaches different limits at the three vulcanization temperatures, so that the curves cannot be superposed merely by an adjustment of the time scale. Although, for this reason, a temperature coefficient cannot be simply obtained from the yield-temperature curves, the crossing over of these curves at the lower vulcanization times suggests that at the lower temperature the rate of vulcanization is lower than was intended, *i.e.*, that too low a value of the temperature coefficient has been adopted. This appears to be supported to some extent by the free sulfur figures for Mixing G, but not for Mixing F; it will be noted, however, that there is no exact correspondence between yield temperature and percentage of free sulfur.

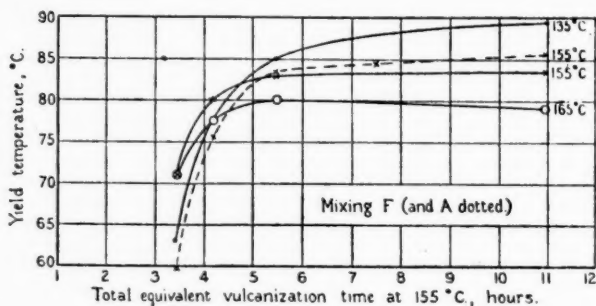


Fig. 1.—Influence of equivalent vulcanization time on the plastic yield temperature of Mixing F vulcanized at 135°, 155°, and 165° C.

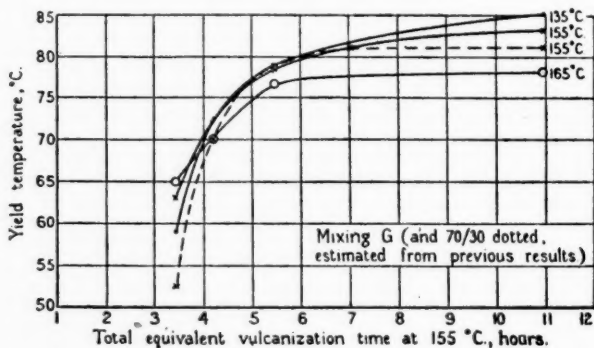


Fig. 2.—Influence of equivalent vulcanization time on the plastic yield temperature of Mixing G vulcanized at 135°, 155°, and 165° C.

RESULTS OF TESTS ON SAMPLES VULCANIZED FOR THE EQUIVALENT OF FIVE HOURS AT 155° C

In the following tables of results the value for A/5 hours and the estimated value of a 70/30 mixing vulcanized for 5 hours at 155° C from the earlier work¹ will be included for comparison as before. Where tests were carried out on samples vulcanized by the India Rubber, Gutta-Percha and Telegraph Works Co., these results will be quoted together with those obtained on the R.A.B.R.M. samples, and will be distinguished by the heading I.R.G.P.

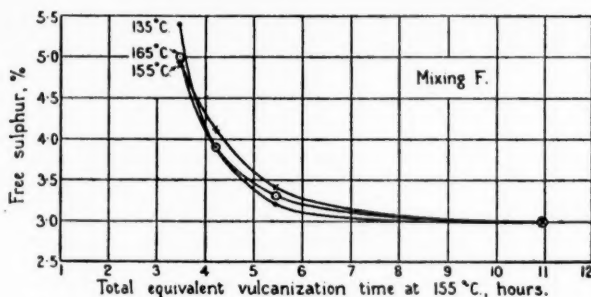


FIG. 3.—Variation of free sulfur with equivalent vulcanization time. Mixing F vulcanized at 135°, 155°, and 165° C.

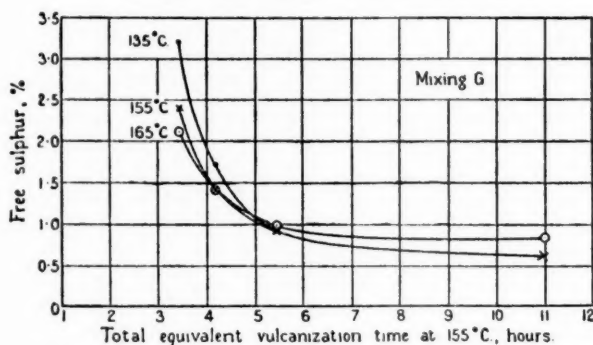


FIG. 4.—Variation of free sulfur with equivalent vulcanization time. Mixing G vulcanized at 135°, 155°, and 165° C.

TABLE 3
DENSITY AT 15° C

Sample	Density (g. per cc.)
F/165° C	1.196
F/155° C	1.197
(A/5 hour)	(1.199)
F/135° C	1.195
G/165° C	1.162
G/155° C	1.161
(70/30 estd.)	(1.161)
G/135° C	1.160

TABLE 4
CROSS-BREAKING STRENGTH AND ELONGATION

Sample	Cross-breaking strength (kg. per sq. cm.)	Cross-breaking "elongation" (%)
F/165° C	1506	10.6
F/155° C	1470	10.3
(A/5 hour)	(1507)	(11.2)
F/135° C	1450	10.5
G/165° C	1345	12.2
G/155° C	1380	12.2
(70/30 estd.)	(1400)	(12.3)
G/135° C	1390	11.4

TABLE 5
IMPACT STRENGTH BY METHOD 2

Sample	Strength (notched) (kg.-cm. per sq. cm.)		Strength (unnotched) (kg.-cm. per sq. cm.)	
	R.A.B.R.M.	I.R.G.P.	R.A.B.R.M.	I.R.G.P.
F/165° C	3.30	—	55	—
F/155° C	1.53	3.1	56	59
(A/5 hour)	(2.00)	—	(55)	—
F/135° C	1.46	2.7	20	52
G/165° C	2.57	—	60	—
G/155° C	2.69	3.2	64	69
(70/30 estd.)	(2.7)	—	(63)	—
G/135° C	3.03	3.1	43	47

DENSITY

(1) The figures are in good agreement with those of the earlier work¹ and with the theoretical values, indicating that there is no serious microporosity.

(2) There is no appreciable variation of density with vulcanization temperature. This is in accordance with the results of McPherson².

CROSS-BREAKING STRENGTH AND ELONGATION

(1) The results obtained with a vulcanization temperature of 155° C agree well with those of the previous work¹.

(2) The variation in cross-breaking strength with vulcanization temperature is not significant relative to the error of measurement; in any case it is so small as to be of little practical importance and is in opposite directions for the two mixings. There is no significant variation in cross-breaking elongation.

IMPACT STRENGTH

The method of determining impact strength was that referred to in the earlier work¹ as Method 2, *i.e.*, where each sample was subjected to a series of blows increasing in magnitude by regular steps. The results of tests on materials prepared at both laboratories are shown in Table 5.

On the main issue, the influence of vulcanization temperature, these results are not conclusive, and some repetition would be desirable to confirm the indications; but there are some points which call for comment.

(1) When only the R.A.B.R.M. materials were tested, it appeared that Mixing F vulcanized at 135° C was much inferior to the same mixing vulcanized at 165° C, whether tested notched or unnotched. The density gave no indication of porosity, but examination of the broken test-pieces showed a few isolated crystals of sulfur (diameter 0.5–1 mm.). Smaller crystals were not found, even on microscopical examination of the cut interior, and the low impact values were not confined to the individual samples in which crystallization was visible. It was thought at first that this crystallization resulted from imperfect mixing, but it did not occur at all vulcanizing temperatures with the same stock. Other suggestions were that the low impact strength was due to frequent interruptions in vulcanization or to the prolonged vulcanization at a low temperature, either of which might favor migration and internal crystallization of sulfur. (It was noted that there was very heavy blooming of sulfur in this particular sample immediately after the preliminary molding, when it was in a soft leathery condition.) It was therefore decided to repeat

the vulcanization of certain samples without interruption, except between the preliminary and final molding. The second set of figures (I.R.G.P.) in Table 5 show the results on the repeated samples.

In every case there is an improvement, which is particularly marked in the high-sulfur Mixing F, and especially when vulcanized at 135° C. The improvement is not entirely explained by the less frequent interruption in vulcanization, since the samples vulcanized at 155° C had the minimum number of rises (two) in all cases, and there is an improvement of these samples also.

As was pointed out earlier¹, impact strength appears to be very sensitive to untraced variables in manufacture, and it would be advisable before any further work on vulcanizing temperature to make some study of the influence of molding procedure on impact strength. Such a study, besides removing variables which complicate the interpretation of experimental results, might well result in a general improvement in the impact strength of hard rubber.

(2) The general indication is that vulcanization at 135° C is not advantageous so far as impact strength is concerned. In the unnotched test-pieces, both sets of samples show an inferiority at 135° C, but the difference between 155° and 165° C is negligible. In the notched test-pieces the results are not very regular, but there are suggestions that the 65/35 mixing improves in impact strength with increasing temperature of vulcanization, while the 70/30 mixing varies in the opposite direction. As these effects are within the limits of experimental error, more tests would be needed to establish their reality. If they were confirmed it might be significant that cross-breaking strength showed trends in the same direction.

(3) In the case of vulcanization at 155° C, the values obtained in the R.A.B.R.M. vulcanization agree well with those obtained in the previous investigation except in notched samples of Mixing F; but the samples vulcanized continuously (I.R.G.P.) are stronger.

PLASTIC YIELD TEMPERATURE

As in the previous experiments¹, the yield temperature was determined by plotting yield against temperature and finding the intercept of the linear portion of the curve on the temperature axis. Table 6 shows the yield tempera-

TABLE 6
YIELD TEMPERATURE AND SLOPE

Sample	Yield temperature (° C)		Slope (angular) degrees/10° C)
	R.A.B.R.M.	I.R.G.P.	R.A.B.R.M.
F/165° C	80	—	10.75
F/155° C	83	81.5*	8.6
(A/5 hour)	(83.2)	—	(8.1)
F/135° C	85	—	6.85
G/165° C	76.5	—	8.9
G/155° C	78.5	77.5*	7.8
(70/30 estd.)	(79)	—	ca. .9
G/135° C	79.0	—	7.75

* Approximate only, since material was tested at two temperatures only.

ture for vulcanization times equivalent to 5 hours at 155° C, and the yield at 10° C above the yield temperature, this figure representing the slope of the linear portion of the curve.

The chief points to be noted from Tables 2 and 6 and Figures 1 and 2 are as follows.

(1) The yield temperature of Mixing G is consistently a few degrees lower than that of Mixing F.

(2) The yield temperatures on vulcanization at 155° C agree well with the values obtained earlier¹.

(3) As the vulcanization temperature decreases, the yield temperature at vulcanization times equivalent to 5 hours or more at 155° C increases continuously. With the shortest vulcanization periods, long before the yield temperature has approached a final value, the reverse is the case, suggesting that a slightly greater temperature coefficient than 2.3 should have been adopted for estimating equivalent vulcanization times. The higher the vulcanization temperature, the more sharply does the yield temperature appear to approach a constant value: in fact, at the lowest temperature the form of curve suggests that the yield temperature may increase considerably on still more prolonged vulcanization. In this connection it may be pointed out that a similar increase in yield temperature on prolonged heating at 70° C has been observed³. In that case the heating was in air, but, as the influence of oxygen during such a period of exposure is confined to the surface, it is probable that there is no difference in the nature of the change in the two cases.

(4) The performance of the samples vulcanized at low temperatures is even better than is shown by the yield temperature, for the slope of the linear portion of the temperature-yield curve decreases with decreasing vulcanization temperature. For example, as seen from Table 6, the yield of F/135° C at 95° C is only about two-thirds of that of F/165° C at 90° C. The change in slope is less marked with Mixing G.

The significance of these effects of vulcanizing temperature on resistance to plastic deformation have been discussed more fully by Porritt⁴.

PERMITTIVITY AND POWER FACTOR AT AUDIO AND RADIO FREQUENCIES

These properties were tested at the National Physical Laboratory, and the following description of the method of testing and the results obtained are taken from the report of the Laboratory.

Six samples (two mixings, three vulcanization temperatures) were tested at temperatures of 17°, 60°, and 80° C, and at frequencies of 800 and 1,000,000 cycles per second.

The samples, on being received at the Laboratory, were cut into circles 22 cm. in diameter, and the two surfaces were ground to a plane on sheets of emery cloth attached to a flat surface. This was necessary so as to be able to define the thickness of the samples with sufficient precision. No more of the surface was removed than was sufficient to render the samples reasonably flat. The samples were then left for the two months preceding the tests in a chamber maintained at a relative humidity of 75 per cent.

The measurements were undertaken on a Schering bridge, using mercury electrodes incorporating a guard-ring device. The temperature of 17° C was substituted for 20° C, which was originally intended, since it was the temperature at which the samples had been stored and which was exactly reproducible for the initial measurements.

The behavior of one specimen at the telephonic frequency (Mixing F, vulcanization temperature 135° C) was unexpected, the power factor at 80° C

showing a distinct fall which remained unchanged overnight. A repetition of the measurements for descending temperatures at 61° and 19° C indicate that the material itself had not changed appreciably. Readings taken at the low temperature two days later on remounting the sample agreed with the original value.

In Tables 7 and 8 the results are grouped under temperatures of test which approximate one another, but where two or more results at one approximate temperature occur the figures are given in the order in which the measurements

TABLE 7
PERMITTIVITY AND POWER FACTOR AT 800 CYCLES PER SECOND

Sample and rubber-sulfur ratio	Temperature of test (° C)	Permittivity for vulcanization temperature			Power factor (%) for vulcanization temperature		
		135° C	155° C	165° C	135° C	155° C	165° C
F65/35	17	2.96	2.93	2.94	0.67	0.51	0.65
	19	2.97	—	—	0.74	—	—
	17	2.97	—	—	0.68	—	—
	60	(2 days later) 3.08	3.02	3.04	(2 days later) 1.41	1.15	1.34
	61	3.08	—	—	1.35	—	—
	80	3.14	3.10	3.12	1.28	1.75	1.49
	77	3.13	—	—	1.28	—	—
	17	2.93	2.90	2.94	0.71	0.50	0.76
	60	3.04	2.98	3.05	1.40	1.10	1.19
	70	3.08	—	—	1.55	—	—
G70/30	80	3.13	3.08	3.16	1.75	1.88	1.55

TABLE 8
PERMITTIVITY AND POWER FACTOR AT 1,000,000 CYCLES PER SECOND

Sample and rubber-sulfur ratio	Temperature of test (° C)	Permittivity for vulcanization temperature			Power factor (%) for vulcanization temperature		
		135° C	155° C	165° C	135° C	155° C	165° C
F65/35	17	2.87	2.85	2.85	0.87	0.85	0.86
	19	2.88	—	—	0.91	—	—
	20	—	(2.86)	—	—	(0.83-6)	—
	60	2.93	2.88 (2.91)	2.90	1.17	1.11 (1.04)	1.14
	61	2.92	—	—	1.16	—	—
	80	2.95	2.92	1.33	1.28	1.28	1.34
	77	—	—	—	1.32	—	—
	17	2.83	2.82	2.84	0.96	0.93	0.99
G70/30	20	—	(2.82)	—	—	(0.91)	—
	60	2.88	2.87 (2.87)	2.90	1.29	1.17 (1.12)	1.35
	70	2.90	—	—	1.37	—	—
	80	2.92	2.90	2.93	1.50	1.38	1.65

were made. As before, comparable results from the previous work¹ are given in brackets for comparison. The figures given in this way for the 70/30 mixing are estimated by interpolation between those obtained with the 68/32 and 72/28 mixings.

Permittivity and power factor at 800 and 10⁶ cycles per second respectively are plotted against temperature of test in Figures 5, 6, 7, and 8.

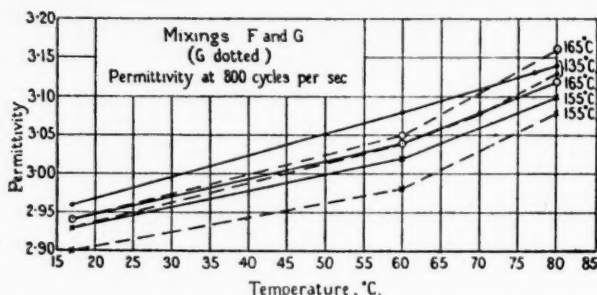


Fig. 5.—Influence of temperature of test on the permittivity at 800 cycles per sec. of Mixings F and G vulcanized at 135°, 155°, and 165° C.

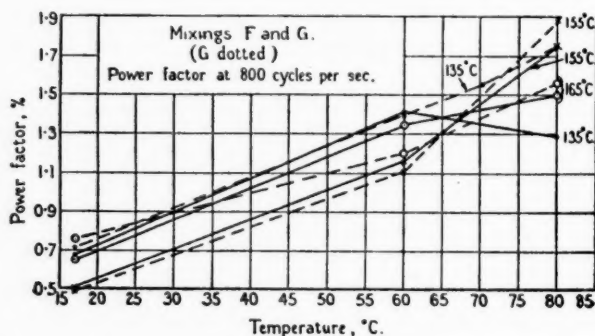


Fig. 6.—Influence of temperature of test on the power factor at 800 cycles per sec. of Mixings F and G vulcanized at 135°, 155°, and 165° C.

DISCUSSION OF RESULTS

Although this investigation is concerned primarily with the influence of temperature of vulcanization, the results afford information on a number of other variables, principally rubber-sulfur ratio, frequency, and temperature of test. These relations may conveniently be discussed first. Further, the variations of power factor and permittivity at the radio frequency are of primary practical importance, the variations of these properties at the telephonic frequency being of interest chiefly in relation to the question of the use of low-frequency tests in predicting properties at radio frequency. It is proposed, therefore, not to discuss the telephonic frequency tests in detail except under the heading of influence of frequency.

The whole question of the relations between power factor and permittivity on the one hand, and frequency, temperature and composition on the other, has been very fully investigated by Curtis, McPherson, and Scott⁵, Boggs and Blake⁶, and Kitchin⁷. In this discussion, although general comparisons will be made with the work of these investigators, exact numerical comparisons cannot be made because their work differed in the following important respects from the present work.

(1) Their tests were made at very low relative humidity, whereas these were made at 75 per cent relative humidity. It is known that absorbed moisture

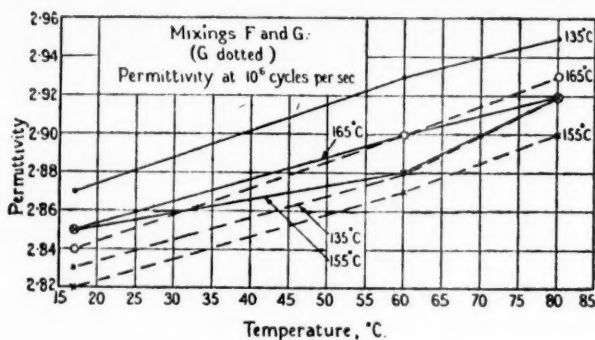


Fig. 7.—Influence of temperature of test on the permittivity at 10^6 cycles per sec. of Mixings F and G vulcanized at 135°, 155°, and 165° C.

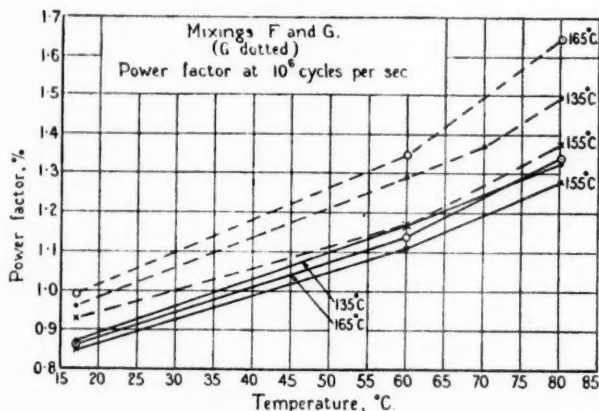


Fig. 8.—Influence of temperature of test on the power factor at 10^6 cycles per sec. of Mixings F and G vulcanized at 135°, 155°, and 165° C.

greatly affects the electrical properties, and to different extents at low and high frequencies.

(2) Their materials were made from different mixings vulcanized either for a fixed time or until free sulfur was negligible, whereas in one mixing reported here there was more than 3 per cent of free sulfur.

(3) Kitchen's results, which extend to 2000 kc. per sec., do not refer to materials with more than 28.41 per cent of combined sulfur, and the results of Curtis, McPherson and Scott⁵, which extended to nearly 32 per cent of combined sulfur, were tested only up to 300 kc. per sec. The material used in the latter case was made from purified rubber instead of commercial rubber.

Agreement with previous results¹

(i) Permittivities at 10^6 cycles per second are in good agreement with those of the previous part of the investigation¹.

(ii) Power factors are in good agreement also at room temperature, but a little higher than before at 60° C.

Influence of frequency

(1) As usual, the permittivity decreases with increasing frequency (by about 3 to 7 per cent). The change is slightly greater with mixing G (70/30) and shows a slight but consistent minimum at a temperature of vulcanization of 155° C for all temperatures of test and both mixings.

(2) At room temperature power factor increases considerably with increasing frequency, the increase being about twice as great with a vulcanization temperature of 155° as for 135° or 165° C. This maximum effect for 155° C is mainly due to a marked minimum of power factor at 800 cycles per sec., not to any large variation of power factor at 10⁶ cycles per second.

At higher test temperatures the influence of frequency is, on the whole, in the opposite direction and does not appear to be simply related to either rubber-sulfur ratio or temperature of vulcanization.

These relations may be seen in Table 9, where power factors at both frequencies are tabulated, each pair of figures being the result obtained at 800 cycles per sec. above that at 10⁶ cycles per second, and the ratio being added in brackets.

TABLE 9
INFLUENCE OF FREQUENCY ON POWER FACTOR

Sample and rubber-sulfur ratio	Temperature of test (° C)	Power factors (%) at two frequencies, and ratio of same at vulcanization temperature					
		135° C		155° C		165° C	
F65/35	17	0.67	(1.30)	0.51	(1.67)	0.65	(1.32)
	60	0.87		0.85		0.86	
		1.41	(0.83)	1.15	(0.96)	1.34	(0.85)
	80	1.17		1.11		1.14	
		1.28	(1.04)	1.75	(0.73)	1.49	(0.90)
		1.33		1.28		1.34	
G70/30	17	0.71	(1.35)	0.50	(1.75)	0.76	(1.30)
	60	0.96		0.93		0.99	
		1.40	(0.92)	1.10	(1.06)	1.19	(1.13)
	70	1.29		1.17		1.35	
		1.55	(0.88)	—		—	
	80	1.37					
		1.75	(0.86)	1.88	(0.73)	1.55	(1.06)
		1.50		1.38		1.65	

Influence of temperature of test

(1) Permittivity at 10⁶ cycles per sec. increases between 17° and 80° C with a temperature coefficient of about 0.0012/° C. This is only about one-half as great as the coefficient for 800 cycles per second.

(2) Power factor at 10⁶ cycles per sec. increases between 17° and 60° C with a temperature coefficient of about +0.000078/° C, compared with about 0.00016/° C at 800 cycles per second. The rate of increase with temperature is greater between 60° and 80° C. The lower temperature coefficient at the higher frequency is consistent with the work of the previous investigators mentioned above.

It may be mentioned here that at 800 cycles per sec. one specimen (F/135° C) shows a decrease of power factor from 60° to 80° C. Such a maximum has been found under various conditions of test with various rubber-sulfur compositions, *e.g.*, by Kitchen⁷ and by Curtis, McPherson, and Scott⁸, and has been

shown to be consistent with a dipole theory of dielectric loss, the polarity of the molecule increasing with the percentage of combined sulfur. The present tests would indicate that, with mixings vulcanized to the same extent, judged by combined sulfur, the conditions (temperature and test frequency) at which the maximum occurs depend on the temperature of vulcanization. It is recommended that confirmation of this effect should be sought with new material. If the effect is genuine it is of great scientific interest, for it implies that the temperature of vulcanization affects the polarity of the rubber-sulfur molecules and(or) the intermolecular forces that hinder dipole movements, although the percentage of combined sulfur remains constant. In this connection the part which may be played by absorbed moisture and nonrubber components of the rubber must be borne in mind, since these might be affected by the temperature of vulcanization.

Influence of rubber-sulfur ratio

(1) At 10^6 cycles per sec. the permittivity does not vary seriously with composition. Although the results for the three samples of Mixing G lie as a group lower than those of Mixing F, the differences are so small as to be of little practical importance.

(2) At 10^6 cycles per sec. the power factors of Mixing G are definitely higher at all temperatures of test and temperatures of vulcanization than those of Mixing F. This is in agreement with the results of the previous work¹. At 800 cycles per sec. the mixings do not differ systematically.

Influence of temperature of vulcanization

(1) At 10^6 cycles per sec. the permittivity varies only slightly with the temperature of vulcanization, but at all temperatures and with both mixings, there is a minimum for a vulcanization temperature of 155°C . A similar minimum is observed at 800 cycles per sec.

(2) At 10^6 cycles per sec. the power factor is less at a vulcanization temperature of 155° than at 135° or 165°C , especially at the higher temperatures of test. The minimum is more marked with Mixing G than with Mixing F. There is a similar but much more marked minimum at 800 cycles per sec. at temperatures up to 60°C , above which there is an equally marked maximum.

SURFACE DISCOLORATION IN SUNLIGHT

Samples of each mixing, vulcanized at the three temperatures for the equivalent of 5 hours at 155°C , were exposed to daylight for six months and the resultant discoloration observed. As in the previous work¹, the color was intensified by dipping the samples for a few seconds into boiling water. It was found, as before¹, that samples G were intensely colored and F less so, but there was no visible influence of the temperature of vulcanization.

GENERAL DISCUSSION ON CHOICE OF VULCANIZATION TEMPERATURE

The principal effects of varying the vulcanization temperature may now be briefly summarized as follows:

Free sulfur.—There is no difference in percentage of free sulfur after allowance is made for the difference in rates of vulcanization.

Density.—There is no sensible difference.

Cross-breaking strength.—There is no significant difference, certainly none of practical importance.

Impact strength.—The results tend to show that the materials vulcanized at 135° C are inferior to the others, but it is suspected that this may be a secondary effect which could be avoided by proper attention to mixing and vulcanizing technique. Judgment on this point must, therefore, be suspended until an investigation as to the effects of variables in mixing and vulcanizing has been carried out.

Yield temperature.—Yield temperature increases considerably (by 7°–10° C) as the temperature of vulcanization is decreased. At the highest temperature the yield temperature approaches a limit during vulcanization more definitely than at the lower temperatures.

Dielectric loss.—Both permittivity and power factor results are lower at 155° than at 135° or 165° C. The effect varies in magnitude with both composition and temperature of test. At room temperature the minimum is not very marked, but at higher temperatures (60°–80° C) it is quite appreciable, especially with the low-sulfur mixing.

Surface discoloration.—In sunlight the discoloration occurs almost equally whatever the temperature of vulcanization within the range 135°–165° C. Electrical tests of the rate of deterioration have not been made, but in the previous part of the investigation close correspondence has been observed between rates of discoloration and of fall in surface resistivity.

The selection of the best temperature of vulcanization is therefore a difficult question involving compromise between opposing tendencies in the different properties. Apart from the increase in cost due to the longer vulcanization time, a decrease in temperature improves resistance to plastic flow but possibly results in a lower impact strength, while the dielectric loss passes through an optimum value.

SUMMARY

In previous reports⁸ the properties of hard rubber made from rubber and sulfur were studied with particular reference to the effects of varying the rubber-sulfur ratio and vulcanization time. In the present report, a continuation of this investigation, the influence of temperature of vulcanization of similar materials is studied.

Materials having rubber-sulfur ratios of 65/35 and 70/30 were vulcanized in a press at three different temperatures, namely, 165°, 155°, and 135° C, the times of vulcanization employed being estimated to be equivalent to 5 hours at 155° C.

As a check on the estimate of the equivalent times, small samples of the same materials were vulcanized for various shorter and longer periods and were tested for plastic yield temperature and percentage of free sulfur.

The main materials were tested for the following properties by the methods described in the previous report: Combination of sulfur, density, cross-breaking strength and elongation, impact strength, plastic-yield temperature, permittivity and power factor at audio and radio frequencies, and surface discoloration in sunlight.

Certain anomalous figures were obtained in the impact test results which were thought to be due to the necessity of carrying out the longer vulcanization processes in stages. Arrangements were made accordingly to conduct the vulcanization continuously in such cases. This procedure brought about a

considerable improvement in the results. These results confirmed the conclusion reached in the previous report that impact strength is very sensitive to untraced variables in manufacture.

The results of the permittivity and power factor tests are discussed at some length, since they afford useful information on a number of other variables, principally rubber-sulfur ratio, frequency, and temperature of test.

In a general discussion of the results, the choice of the best vulcanization temperature is examined. It is concluded that the selection of the best temperature involves compromise between opposing tendencies in the different properties.

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PROPERTIES OF HARD RUBBER. XXII. DEVELOPMENT OF PROOF IMPACT TEST FOR INSULATING MATERIALS. COMPARISON OF PENDULUM AND FALLING-WEIGHT MACHINES *

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INTRODUCTION

The object of the investigation was to compare the pendulum and falling-weight types of impact testing machine, using four different materials (synthetic-resin paper board, synthetic-resin fabric board, synthetic-resin molding, and ebonite) and with each material four types of test-piece (unnotched, saw-cut notch, and two types of V-notch). With the falling-weight machine, tests have been made both by the Izod method (specimen mounted as a cantilever) and the Charpy method (specimen supported at ends and struck in the center). With the pendulum machine only the Izod method has been used.

The investigation includes also a preliminary set of tests with the pendulum machine to determine the effect of varying the striking distance, *i.e.*, the distance between the clamp and the point of impact.

DESCRIPTION OF TESTING MACHINES AND METHODS OF USE

Both the machines were specially constructed for this investigation from designs prepared by H. F. Church, of the Electrical Research Association.

PENDULUM MACHINE (*See Figure 1*)

To cover the very wide range of impact blows necessary, the machine is provided with two pendulums, A for the heavier blows and B for the lighter blows. The angular movements of pendulums A and B are indicated, respectively, on the scales C and D, each of which bears, in addition to a scale of degrees, a scale of percentage excess energy as measured by the swing-through of the pendulum after breaking the specimen. The pointer is moved over the scale by an arm connected to the pendulum, and thereafter remains in position so as to indicate the percentage excess energy in the pendulum.

Both pendulums are arranged to fall through a vertical distance of 57.36 cm., giving a striking velocity of 11 ft. (335.3 cm.) per sec. The pendulums are mounted on Hoffmann journal bearings.

Each pendulum is provided with a series of detachable pairs of weights (some are shown at E in Figure 1) which are so shaped and attached that the center of percussion of the pendulum always remains in the center of the striking edge. This edge is horizontal and is rounded to a radius of $\frac{1}{8}$ inch.

* Reprinted from the *Journal of Rubber Research*, Vol. 16, No. 4, pages 104-122, April 1947. This report gives the results of an investigation carried out on behalf of the British Electrical and Allied Industries Research Association to provide data for use in developing a standard proof contact test for insulating materials.

The specimen *F* is held vertically between clamps which are made so that the striking distance can be varied. Unnotched specimens are fixed with the center of their length level with the top surface of the clamps, and notched specimens with the notch level with this surface and on the face which receives the blow. All specimens of laminated materials were placed so that the struck face corresponded to the original surface of the sheet.

The machine was fixed down to four bolts embedded in a heavy concrete block.

To calibrate the machine, the effective weight of each pendulum was determined as follows. The pendulum was supported in a horizontal position by resting the striking edge on a rounded rod perpendicular to it. The rod

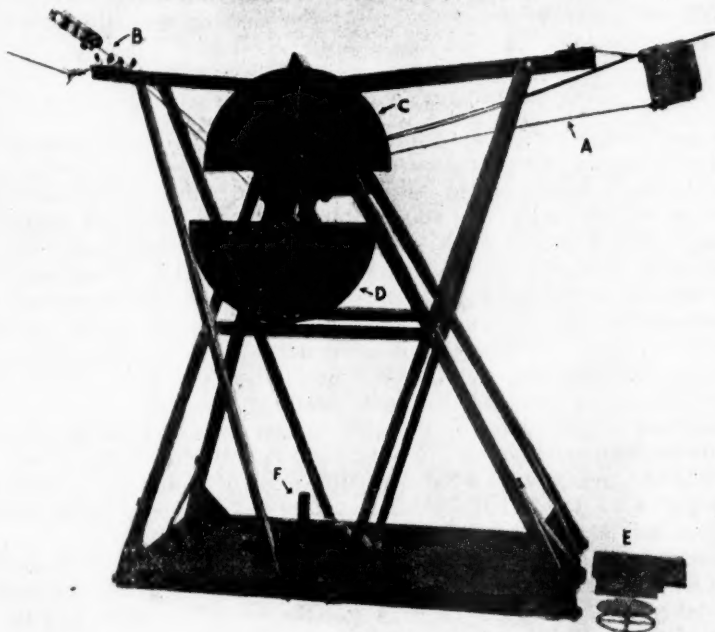


FIG. 1.—Pendulum type impact testing machine.

was carried by one arm of a balance; weights were placed in the pan on the other arm until the pendulum just moved up (weight = W_1), and then removed until it just moved down again (weight = W_2). The effective weight of the pendulum was taken as the mean of W_1 and W_2 . The process was carried out with each of the pairs of detachable weights in position.

The impact strength of the specimen was calculated from the initial energy in the pendulum and the percentage excess energy indicated by the pointer on scale *C* or *D* after the pendulum had broken the specimen. Corrections were applied for friction and windage, these being determined as follows. The pointer was set to zero, and the pendulum allowed to swing from its normal starting position without a test-piece in the clamps; the percentage excess

energy was read off ($=x$). Without readjusting the pointer the pendulum was allowed to swing several times in succession until the pointer moved no further; final reading $= y$ (x and y were determined, for every combination of weights used, immediately before each set of tests). The pointer was then readjusted to zero, the specimen placed in position, the pendulum allowed to fall, and (if the specimen broke), the final reading of the pointer taken ($=z$).

The energy of break (E_b) was then calculated by the formula:

$$E_b = (E_1\sqrt{y}/10)(1 - z/x),$$

where E_1 = initial energy of pendulum ($=$ calibration weight \times 57.36 cm.). The derivation of this formula is given in Appendix I. The impact strength is the energy of break divided by the cross-sectional area of the specimen.

The tests were arranged, so far as possible, so that the excess energy did not exceed 25 per cent of the initial energy, this limit having been stipulated by the Committee responsible for the investigation.

FALLING-WEIGHT MACHINE (See Figure 2)

The machine, which is an improved form of that already described by Church and Daynes¹, consists of a striker A sliding between two vertical guides BB and having a striking edge rounded to $\frac{1}{8}$ inch radius. It is loaded with weights as required. For the smaller impact blows, two light strikers are provided, together with a set of smaller weights. For the Charpy test, the specimen G is supported near its ends by two supports HH, 70 mm. apart and having their edges rounded to 1/16 inch radius. The specimen is struck midway between the supports on a face corresponding to the original surface of the sheet, and the notch (if any) is on the under side directly beneath the point of impact. For the Izod test the specimen is held in clamps replacing the supports HH, in the same way as in the pendulum machine.

The striker is held by a catch J on the bottom end of the rod K, which can be slid up or down and fixed at any position to vary the fall of the striker. All the tests in the present work were made with a fall of 57.36 cm., corresponding to an impact velocity of 11 ft. (335.3 cm.) per sec. The machine is built on a heavy cast iron base L.

In using the machine the method was as follows. A number of specimens (usually six) were struck, each once, with a blow estimated, from the results of a few trial experiments, to be rather below the impact strength, and the percentage of specimens that broke was noted. This procedure was repeated with successively heavier blows (*i.e.*, bigger loads) until a stage was reached where all or nearly all the specimens broke; usually about five different loads were sufficient.

The percentage of breaks was then plotted against the load per unit area of the cross-section of the specimens. From the resulting S-shaped curve the load corresponding to 50 per cent breaks was read off. This load (kg. per sq. cm.) multiplied by 57.36 cm. gives the impact strength (kg. cm. per sq. cm.).

PRELIMINARY TESTS WITH DIFFERENT STRIKING DISTANCES

As a preliminary to the main investigation, the effect of varying the striking distance in the pendulum test was examined.

For this purpose, synthetic-resin fabric board approximately 15 mm. thick was used; this was cut into specimens (unnotched) 80 mm. long and 15 mm.

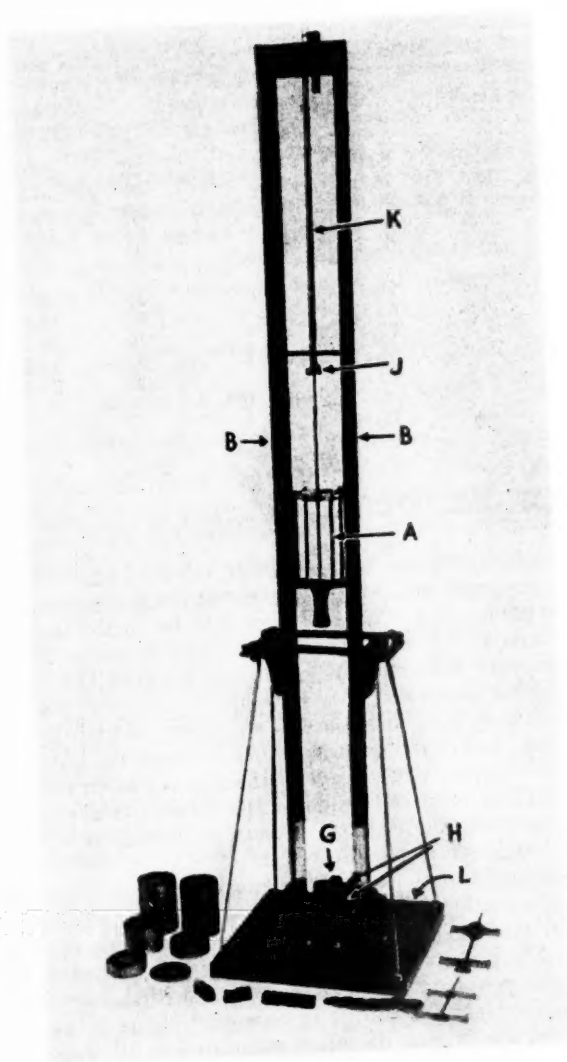


FIG. 2.—Falling-weight type impact testing machine.

wide. These were conditioned for 48 hours at $20^{\circ} \pm 5^{\circ} \text{C}$ and 75 per cent relative humidity. Ten specimens were tested with each of two striking distances, 20 mm. and 35 mm. (see Table 1).

TABLE 1

Specimen no.	Striking distance 35 mm.			Specimen no.	Striking distance 20 mm*.	
	Excess energy (%)	Impact strength (kg. cm. per sq. cm.)	No. of plies unbroken		Excess energy (%)	Impact strength (kg. cm. per sq. cm.)
10	25.0	80.0	†	20	26.9	91.5
11	33.3	70.8	†	21	15.2	101.2
12	30.9	70.0	1	22	30.5	83.1
13	30.9	69.3	1	23	15.6	101.0
14	25.3	65.3	2	24	14.3	102.8
15	7.2	76.4	2	25	33.9	82.4
16	23.8	65.1	2	26	19.8	106.9
17	17.0	72.4	1	28	28.0	85.1
18	26.8	63.2	1	29	13.9	100.8
19	8.2	78.7	2	30	25.9	88.6
Mean	—	71.1	—	—	—	94.3
Average deviation from mean	—	6.5%	—	—	—	8.8%

* All specimens broke completely through.

† The plies remaining unbroken by the impact were broken by the return swing of the pendulum.

The higher impact strength obtained with the 20 mm. striking distance is probably due to the larger component of shear stress in the specimen when this short distance is used. The effect is expected to be particularly marked with laminated materials struck in a direction perpendicular to the laminations. There is no significant difference in variability between the results obtained with the two striking distances.

With the 35 mm. striking distance, the specimens did not break completely through, but a few plies of fabric on the far side remained unbroken, as noted in Table 1. This occurred irrespective of the amount of excess energy, at any rate up to the highest observed value of the latter (33 per cent), though it seems probable that with more than a certain percentage of excess energy the specimen would break completely through.

It might be thought that as the whole cross-sectional area is not broken through, the results would be low. There is no direct evidence of this, however, as both high and low results are obtained with specimens showing the same number of unbroken plies, and the specimens with 2 unbroken plies actually give no lower average impact strength than those with 1 unbroken ply.

In cases of incomplete fracture it is necessary, so as to avoid jarring the pendulum, to catch the bob on its return swing before allowing the pendulum to return to the vertical. The 20 mm. striking distance is therefore preferable as regards ease of manipulation.

In all cases the breaks were quite irregular, the fabric often tearing out for some distance below the top of the clamp on the struck side of the specimen.

With the fabric board used, it was practically impossible to keep the excess energy below 25 per cent, because the variation among the strengths of individual specimens was of the order of 25 per cent; thus, a blow which would

just break the strongest specimen would have given 23 per cent (at 20 mm. striking distance) or 21 per cent (at 35 mm.) excess energy with the weakest, so that it would be very difficult to choose a blow that would break every specimen and yet never give more than 25 per cent excess energy.

In the tests with 35 mm. striking distance, specimens Nos. 10 to 13 were given a heavier blow (about 105 kg. cm. per sq. cm.) than Nos. 14-19 (about 85 kg. cm. per sq. cm.), so the excess energy was greater with the former. The mean impact strengths for these groups are: Nos. 10-13: 72.5 kg. cm. per sq. cm.; Nos. 14-19: 70.1 kg. cm. per sq. cm.

Since the difference between these figures is not significant relative to the variation between individual results in each group, there is no definite evidence that the impact strength result depends on the magnitude of the blow used and hence on the average excess energy in the pendulum.

The excess energy question is discussed more fully in the following section under the subject of the excess energy in pendulum tests in the discussion of the results.

IV. MAIN INVESTIGATION

MATERIALS AND TEST-PIECES USED

The following materials were tested:

Synthetic-resin fabric board (heavy type).

Synthetic-resin paper board, Grade I (Paxolin).

Synthetic-resin molding (Bakelite) made from powder similar to X20.

Ebonite to comply with B.S. 234-1933.

Each was examined in the following types of test-piece:

(1) Unnotched: bar 80 mm. long and $\frac{1}{2}$ -inch square cross-section.

(2) Saw-cut notch: as (1) but with notch formed by drilling a hole of 2 mm. diameter through the specimen (in middle of length) with the bottom of the hole 0.4 inch (10.16 mm.) from one face of the specimen, and then making a cut with a saw from the opposite face down to the hole.

(3) Large V-notch: as (1) but with notch formed by drilling a 2 mm. hole as in (2) and completing the notch with a V-tool of 45° angle, so that the sides of the notch are tangential to the hole.

(4) Small V-notch: as (3) but starting with a hole 1 mm. diameter.

The paper board, ebonite, and Bakelite were received in the form of pieces of nominally the required size, except that the Bakelite specimens were slightly too long and had to be shortened. The fabric board was received as bars nominally $\frac{1}{2}$ -inch square from which specimens of the required length were cut off. To ensure uniformity, all the specimens of fabric board and paper board were cut from one sheet, from which a 6 inch wide edge had first been removed.

A drill revolving at 480 r.p.m. was used for making the holes, the best angle for the conical end of the drill being found to be as follows: Fabric board 80°, paper board 60°, Bakelite 90°, ebonite 60°. Some trouble was experienced with splitting of the paper board and chipping of the Bakelite during drilling, and with chipping of the paper board, Bakelite, and ebonite in machining out the notches.

Data relating to the cross-sectional dimensions of the specimens are summarized in Table 2. The values stipulated by the Committee for both width

and thickness (unnotched specimens only) were 12.7 mm., ± 0 , -5 per cent (*i.e.*, 12.07 to 12.7 mm.).

Most of the specimens lie within the specified limits for width and thickness. As impact strength per unit cross-sectional area is independent of width, the variations shown in Table 2 cannot have any appreciable effect on the results. Variations in thickness affect strength more seriously, but as the greatest deviation above the allowable maximum thickness is only 1.1 per cent in Table 2, and the greatest variation in thickness for any one material is barely 6 per cent, it is not considered that this variation invalidates the results.

TABLE 2
ALL DIMENSIONS IN MM.

Dimension	Material	Specimen	Highest	Lowest	Mean
Width	Fabric board	Unnotched	12.69	12.50	12.64
		Saw-cut notch	12.68	12.60	12.64
		Large V-notch	12.70	12.60	12.65
		Small V-notch	12.68	12.60	12.64
	Paper board	Unnotched	12.95	12.36	12.63
		Saw-cut notch	12.84	12.28	12.61
		Large V-notch	12.78	12.39	12.61
		Small V-notch	12.97	12.00	12.60
	Bakelite	Unnotched	12.60	12.38	12.44
		Saw-cut notch	12.52	12.43	12.48
		Large V-notch	12.52	12.46	12.48
		Small V-notch	12.50	12.40	12.46
	Ebonite	Unnotched	12.71	12.54	12.63
		Saw-cut notch	12.69	12.58	12.64
		Large V-notch	12.68	12.52	12.62
		Small V-notch	12.72	12.59	12.65
Thickness	Fabric board	Unnotched	12.83	12.43	12.65
	Paper Board	Unnotched	12.84	12.10	12.57
	Bakelite	Unnotched	12.62	12.38	12.44
	Ebonite	Unnotched	12.74	12.47	12.58

RESULTS

All specimens were conditioned for 48 hours at $20^{\circ} \pm 5^{\circ}$ C and 75 per cent relative humidity, and tested at temperatures between 13° and 27° C. In the Izod tests on both machines the striking distance² was 22 mm.

The results obtained with the pendulum machine are given in Tables 3-6, in which the following abbreviations are used:

- Ex. En. = excess energy in pendulum (per cent of initial energy).
 I.S. = impact strength (energy of break), kg. cm. per sq. cm.
 NB = no break.

Any samples that did not break completely through or where the excess energy exceeded 25 per cent are given below the mean and are not included in the latter.

The room temperature during the test is given below the name of the test-piece.

TABLE 3
FABRIC BOARD (PENDULUM MACHINE)

	Unnotched 13° C		Saw-cut notch 17° C		Large V-notch 17° C		Small V-notch 18° C	
	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.
	22.2	69.2	5.1	52.8	17.6	47.9	21.3	41.8
	20.5	70.8	21.1	43.7	25.0	41.7	4.3	45.0
	10.0	72.7	21.7	45.2	8.8	46.9	14.0	40.3
	13.0	70.0	7.0	54.0	17.3	46.2	11.4	41.5
	18.8	65.4	22.2	45.2	23.7	42.4	10.7	41.9
	5.4	76.3	24.6	43.7	18.0	45.8	17.0	38.7
	10.6	71.9	17.0	47.1	4.8	50.9	24.8	35.1
	4.4	77.2	22.2	43.3	3.1	51.8	10.9	41.8
	11.8	70.9	8.5	48.8	19.2	42.9	17.1	38.9
	17.0	66.9	13.0	46.3	12.8	46.6	8.8	42.9
Mean	—	71.1	—	47.0	—	46.3	—	40.8
	32.0	65.2	2.3	42.5*	2.8	43.5*	4.4	42.7*
	37.6	57.8	3.2	42.1*	2.8	45.9*	26.0	39.2
			2.5	54.4*	6.3	48.3*	29.0	36.2
			27.2	42.1	5.2	50.6*		
			31.3	39.7	27.1	42.2		
			34.1	34.9	27.8	40.1		
					28.7	37.9		

* Two of three plies of fabric remained unbroken on the side opposite the struck face.

TABLE 4
PAPER BOARD (PENDULUM MACHINE)

	Unnotched 21° C		Saw-cut notch 23° C		Large V-notch 24° C		Small V-notch 23° C	
	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.
	5.5	14.0	8.8	7.42	8.9	6.41	10.5	7.30
	17.7	12.2	10.8	7.23	7.7	6.52	9.8	6.41
	6.1	14.0	17.4	6.68	11.0	6.27	5.4	6.73
	7.0	13.9	18.8	6.55	12.4	6.17	8.8	6.47
	8.0	16.3	8.8	7.40	7.2	6.53	6.3	6.69
	25.0	12.7	19.8	6.45	10.4	6.29	16.2	5.92
	8.6	16.3	16.8	6.72	9.1	6.42	9.0	6.51
			9.4	6.38	9.1	6.42	11.2	6.30
			20.8	5.54	14.3	6.01	9.8	6.40
			6.7	6.62	12.2	6.20	11.2	6.31
Mean	—	14.2	—	6.70	—	6.32	—	6.50
	NB	>15.9	25.8	5.96	28.4	5.82	37.0	5.04
	37.5	10.7	29.6	5.61				
	32.5	11.3						
	29.6	11.9						
	36.0	10.8						
	34.0	11.5						
	39.0	10.3						
	45.8	9.3						
	34.8	11.1						

TABLE 5
 BAKELITE (PENDULUM MACHINE)

	Unnotched 23° C		Saw-cut notch 23° C		Large V-notch 23° C		Small V-notch 22° C	
	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.
	14.9	6.58	23.2	2.62	15.8	2.19	13.8	2.25
	14.8	6.59	24.0	2.42	13.0	2.28	17.6	2.14
	8.3	7.15	16.0	2.18	9.0	2.39	14.7	2.22
	10.5	6.94	17.9	2.13	8.7	2.41	13.4	2.27
	25.0	6.57	15.3	2.21	5.2	2.50	10.4	2.35
	11.4	7.87	11.5	2.31	24.8	1.93	17.8	1.4
	10.2	7.98	13.1	2.27	19.5	2.08	18.4	2.12
	13.7	7.65	10.1	2.35	18.7	2.10	20.4	2.06
14.3	8.35	10.0	2.36	10.8	2.34	12.6	2.29	
12.0	8.54	11.2	2.38	11.9	2.31	10.4	2.34	
Mean	—	7.42	—	2.32	—	2.25	—	2.22
	NB	>7.75	32.4	2.78	NB	>2.54	27.4	1.86
	NB	>7.75	25.5	2.82	30.6	1.75		
	NB	>8.77			28.5	1.82		
	NB	>8.77						

 TABLE 6
 EBONITE (PENDULUM MACHINE)

	Unnotched 24° C		Saw-cut notch 23° C		Large V-notch 24° C		Small V-notch 24° C	
	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.	Ex. En.	I.S.
	17.4	14.5	17.4	4.01	21.1	3.26	19.2	3.35
	23.8	13.0	17.2	3.45	8.3	3.85	23.8	3.13
	14.8	17.8	6.7	3.91	19.2	3.35	14.2	3.26
	14.8	17.7	23.8	3.13	5.6	3.96	8.7	3.49
	10.0	19.0	17.0	3.45	14.6	3.55	10.4	3.41
	6.7	19.4	7.8	3.85	13.0	3.63	19.7	3.02
	8.2	19.0	15.8	3.50	20.4	3.30	21.8	2.94
	19.0	16.9	17.2	3.44	18.7	3.37	20.3	3.00

The results of the falling-weight tests are given in Tables 7-10. With paper board, some of the notched specimens did not break through, but cracked lengthwise, sometimes to one end so that a piece split off. Some fabric board specimens in the Charpy test did not break completely through, but left a few unbroken plies of fabric on the struck side.

In Tables 7 and 8 the percentage of specimens showing any kind of a failure (either a crock or a partial or complete break) has, accordingly, been given in brackets below the percentage that broke right through, and the corresponding value for impact strength is given in brackets below the value corresponding to a complete break through.

In the Izod tests on fabric board none of the specimens broke completely through, as one or two plies of fabric were always left unbroken on the side away from the blow.

TABLE 7
FABRIC BOARD (FALLING-WEIGHT MACHINE)

Specimen	Izod*				Charpy			
	Blow	Sp.	Br.	I.S.	Blow	Sp.	Br.	I.S.
Unnotched	57.4	6	17	60.8*	68.8	6	0	75.7 (74.0)
I: 22° C	58.8	6	17				(17)	
C: 16° C	60.2	6	33		73.1	3	0	
	61.6	6	67				(33)	
	63.1	4	100		73.8	3	0	
	68.8	1	100				(33)	
	74.5	2	100		74.5	7	43	
							(72)	
					77.4	5	60	
							(80)	
					86.1	6	100	
Saw-cut notch	37.3	3	0	40.8*	63.1	7	29	65.4 (63.7)
I: 23° C	40.2	8	88				(43)	
C: 22° C	41.6	8	75		64.5	6	33	
	43.0	8	50				(83)	
	45.9	5	100		66.0	8	63	
							(100)	
					68.8	7	82	
							(100)	
Large V-notch	37.3	5	20	39.6*	57.4	1	0	66.0 (63.1)
I: 23° C	38.2	6	33				(0)	
C: 22° C	38.8	7	71		63.1	5	20	
	40.2	6	67				(60)	
	43.0	8	63		64.5	5	40	
							(60)	
					66.0	8	50	
							(88)	
					68.6	10	70	
							(90)	
					74.6	2	100	
					80.3	3	100	
Small V-notch	34.5	8	25	36.7*	68.2	5	80	67.7 (63)
I: 25° C	35.9	7	29				(80)	
C: 20° C	36.5	5	60		68.8	6	33	
	37.3	6	67				(83)	
	40.2	6	67		69.4	7	71	
	41.6	3	100				(100)	
					70.3	8	63	
							(88)	
					71.7	5	80	
							(100)	
					74.6	6	83	
							(100)	

* All specimens left one or two plies unbroken.

The following abbreviations are used in Tables 7-10.

Blow = energy of blow per unit cross-sectional area of specimen (kg. cm. per sq. cm.).

Sp. = number of specimens tested.

Br. = percentage of breaks.

I.S. = impact strength (energy required to give 50 per cent breaks), kg. cm. per sq. cm.

The test temperature is given below the name of the test-piece; C and I refer to Charpy and Izod tests, respectively.

TABLE 8
PAPER BOARD (FALLING-WEIGHT MACHINE)

Specimen	Izod				Charpy			
	Blow	Sp.	Br.	I.S.	Blow	Sp.	Br.	I.S.
Unnotched	7.46	3	0	8.42*	7.17	6	17	8.50*
I: 25° C	7.75	5	40		7.75	3	0	
C: 16° C	7.91	5	40		8.03	6	17	
	8.03	6	67		8.15	7	29	
	8.61	6	50		8.32	8	63	
	9.18	7	57		8.90	6	67	
					9.47	6	67	
					10.04	6	83	
Saw-cut notch	3.45	3	0	4.08	4.31	6	17	4.63
I: 26° C			(33)	(3.5)†			(50)	(4.45)
C: 22° C	3.73	9	11		4.43	6	33	
			(67)				(33)	
	3.90	6	33		4.59	7	57	
			(67)				(100)	
	4.02	6	50		4.71	7	29	
			(50)				(42)	
	4.31	6	67		4.88	6	83	
			(67)				(83)	
	4.59	3	100					
Large V-notch	1.72	6	0	4.2	4.31	3	0	4.53*
I: 27° C			(0)	(2.05)			(0)	
C: 20° C	2.01	6	0		4.37	5	40	
			(50)				(40)	
	2.29	4	0		4.47	8	75	
			(75)				(75)	
	2.87	3	0		4.59	6	67	
			(100)				(67)	
	3.16	6	0		4.71	6	83	
			(100)				(83)	
	3.45	8	12		4.88	7	57	
			(100)				(57)	
	3.73	3	0					
			(100)					
	4.02	6	67					
			(100)					
	4.59	6	50					
			(100)					
Small V-notch	1.72	5	0	4.02	4.59	4	0	4.87
I: 27° C			(0)	(2.04)			(0)	(4.85)
C: 20° C	1.89	6	0		4.65	2	100	
			(0)				(100)	
	1.95	4	0		4.70	8	38	
			(25)				(38)	
	2.01	6	0		4.76	2	50	
			(33)				(50)	
	2.18	6	0		4.88	9	44	
			(100)				(44)	
	2.29	6	0		4.99	7	57	
			(100)				(71)	
	3.73	3	67		5.17	3	100	
			(100)					
	4.02	6	17					
			(100)					
	4.31	6	83					
			(100)					
	4.59	3	100					

* No incomplete breaks or cracks occurred.

† A repeat set of tests gave 2.0 instead of 3.5.

TABLE 9
BAKELITE (FALLING-WEIGHT MACHINE)

Specimen	Izod				Charpy			
	Blow	Sp.	Br.	I.S.	Blow	Sp.	Br.	I.S.
Unnotched	5.23	6	0	5.39	4.59	1	0	5.42
I: 23° C	5.28	6	17		5.17	3	0	
C: 20° C	5.34	6	33		5.28	5	20	
	5.40	6	50		5.34	6	17	
	5.46	6	67		5.40	5	20	
	5.52	5	80		5.43	3	33	
					5.46	6	83	
					5.74	2	100	
Saw-cut notch	1.72	6	33	1.77	1.15	1	0	1.52
I: 23° C	1.78	9	56		1.44	3	0	
C: 24° C	1.83	6	67		1.46	7	14	
	1.89	7	71		1.49	9	44	
	2.01	3	100		1.55	6	83	
					1.61	6	67	
					1.72	3	100	
Large V-notch	1.55	6	17	1.66	2.12	6	33	2.15
I: 23° C	1.61	6	33		2.18	7	43	
C: 23° C	1.67	6	67		2.21	6	83	
	1.72	7	71		2.24	8	88	
	1.83	6	83		2.30	4	100	
Small V-notch	1.38	6	17	1.49	1.06	3	0	1.15
I: 21° C	1.44	6	33		1.09	9	44	
C: 24° C	1.49	6	50		1.12	9	56	
	1.55	6	83		1.15	8	88	
	1.61	6	100		1.44	6	67	

TABLE 10
EBONITE (FALLING-WEIGHT MACHINE)

Specimen	Izod				Charpy			
	Blow	Sp.	Br.	I.S.	Blow	Sp.	Br.	I.S.
Unnotched	12.6	3	0	13.8	12.6	3	0	16.1
I: 26° C	13.2	6	17		13.8	3	0	
C: 19° C	13.5	6	17		15.0	7	29	
	13.6	5	20		15.5	6	33	
	13.8	8	63		16.1	5	0	
	14.1	7	87		16.6	6	67	
Saw-cut notch	2.01	3	0	2.41	2.01	5	0	2.24
I: 26° C	2.18	6	17		2.12	6	33	
C: 23° C	2.29	7	29		2.18	6	67	
	2.41	7	57		2.30	6	50	
	2.58	6	67		2.58	6	83	
	2.87	3	100		2.87	6	83	
Large V-notch	2.29	6	17	2.58	2.58	2	0	2.77
I: 23° C	2.46	6	67		2.70	6	17	
C: 24° C	2.58	7	29		2.73	3	67	
	2.87	9	56		2.75	6	33	
	2.93	4	100		2.81	7	57	
	2.98	6	100		2.87	6	100	
	3.04	3	100					
Small V-notch	1.72	7	14	1.85	2.18	7	29	2.25
I: 23° C	1.78	6	17		2.30	6	33	
C: 24° C	1.83	7	57		2.35	6	100	
	1.89	8	63		2.41	4	100	
	2.01	6	100		2.46	6	83	
					2.58	6	83	

DISCUSSION OF RESULTS

Mean value of impact strength

The mean impact strength for each material, type of test, and test-piece is shown in Table 11.

TABLE 11
IMPACT STRENGTH (KG. CM. PER SQ. CM.)

Test	Specimen	Fabric board		Paper board	Bakelite	Ebonite
Pendulum, Izod	Unnotched	71.1		14.2	7.42	17.4
	Saw-cut notch	47.0	(46.7)	6.70	2.32	3.54
	Large V-notch	46.3	(46.5)	6.32	2.25	3.51
	Small V-notch	40.8	(41.0)	6.50	2.22	3.18
Falling Weight, Izod	Unnotched		(60.8)	8.42	5.39	13.8
	Saw-cut notch		(40.8)	4.08	1.77	2.41
	Large V-notch		(39.6)	4.20	1.66	2.58
	Small V-notch		(36.7)	4.02	1.49	1.85
Falling Weight, Charpy	Unnotched	75.7	(74.0)	8.50	5.42	16.1
	Saw-cut notch	65.4	(63.7)	4.63	1.52	2.24
	Large V-notch	66.0	(63.1)	4.53	2.15	2.77
	Small V-notch	67.7	(63)	4.87	1.15	2.25

All the figures except those in brackets refer to the energy required to break the specimen right through. In the following cases additional figures, given in brackets, were obtained by including the results for samples that cracked or broke only partially (as explained more fully in the description of the results in this section dealing with the main investigation).

Fabric board.—In the pendulum tests some specimens left a few plies unbroken and in the falling-weight Charpy tests several plies unbroken; in the falling-weight Izod tests all the specimens left one or two unbroken plies.

Paper board.—Some specimens in the falling weight tests cracked, or occasionally broke, lengthwise.

Before considering the results in detail the uncertainty arising from incomplete breaks may be touched upon. With fabric board in the pendulum test, the failure of a few plies to break does not appear to influence the results appreciably (a similar conclusion was indicated by the tests described in the section on preliminary tests with different striking distances). The falling-weight Izod test results for fabric board may therefore be taken as representing approximately the energy required for a complete break, in spite of the fact that one or two plies always remained unbroken.

If, on the other hand, several plies remain unbroken, as in the falling-weight Charpy test, a distinct lowering of the impact strength figure for fabric board results. In these tests values were calculated also for the minimum energy required to produce any visible sign of failure; these were—unnotched 68.8, saw-cut notch 60, large V-notch 62.5, small V-notch 63 kg. cm. per sq. cm.; that is, in general still lower than the values given in the table for an incomplete break.

With paper board the energy required to cause a lengthwise crack or break may be much less than that required for a complete transverse break.

It is evident, therefore, that with laminated materials such as fabric and paper boards the meaning of "break" must be clearly defined if comparable results are to be obtained by different workers.

In the following discussion the figures for complete transverse break only are considered, except with paper board in the falling-weight Izod test, where figures for incomplete break have to be used.

Comparison of different test-pieces

In every case notched test-pieces give lower values than unnotched, though the ratio of notched to unnotched decreases in the order: fabric board, paper board, Bakelite, ebonite. With all four types of test-piece, fabric board is the strongest and Bakelite the weakest material. Of the other two materials, however ebonite is always the stronger in the unnotched form and paper board the stronger in the notched form.

The saw-cut and large V-notches, *i.e.*, those having the same root radius, give nearly the same results (within 7 per cent or less) in all cases except Bakelite and ebonite in the falling-weight Charpy test, and possibly also with paper board in the falling-weight Izod test taking the energy required to produce only a crack (figures in brackets).

In eight cases out of twelve, the small V-notch (0.5 mm. root radius) gives lower values than the large V-notch (1 mm. root radius); in three cases they are practically equal, and in one case the small notch gives the higher figure.

Comparison of the two machines

The pendulum always gives higher results than the falling-weight machine in the Izod test; the ratio is shown in Table 12.

TABLE 12
RATIO OF IMPACT STRENGTH BY PENDULUM TO THAT BY FALLING WEIGHT

	Fabric board	Paper board	Bakelite	Ebonite
Unnotched	1.17	1.68	1.38	1.26
Saw-cut notch	1.15	1.65	1.32	1.46
Large V-notch	1.17	1.50	1.36	1.36
Small V-notch	1.11	1.61	1.49	1.71

The ratio is generally about the same for all forms of test-piece, except that the small V-notched specimen gives higher ratios with nonlaminated materials. The strongest material (fabric board) gives the lowest ratio, but otherwise the ratio bears no obvious relation to the strength of the material.

Although the ratio of pendulum to falling-weight results varies, the two machines always arrange the four materials, in any given form of test-piece, in the same order of merit.

The discrepancy between the pendulum and falling-weight machines is large with some of the materials. Even if results for specimens giving more than 25 per cent excess energy in the pendulum test are included in the mean, the discrepancy is still almost as large. On the other hand it would be somewhat increased if the true value by the falling-weight test could be obtained, because on this machine no correction is made for friction or windage, so that the calculated blow is always greater than that actually delivered to the specimen.

A higher value by the pendulum test is to be expected because the two tests are of a different nature. On the falling-weight machine the minimum energy required to fracture the specimen is observed, whereas on the pendulum machine an excessive blow is applied, and the total energy absorbed by the specimen in breaking is measured. When the bent specimen straightens out at the moment

of rupture, it is likely to react on the pendulum so as to reduce its velocity, thus increasing the measured value of impact strength.

Comparison of Charpy and Izod tests

Comparing these two forms of test, both carried out on the falling-weight machine, it will be seen that in most cases the Charpy test gives the higher result, the difference being most marked with fabric board (see Table 13).

TABLE 13
RATIO OF IMPACT STRENGTH BY CHARPY TEST TO THAT BY IZOD TEST

	Fabric board	Paper board	Bakelite	Ebonite
Unnotched	1.24	1.01	1.01	1.16
Saw-cut notch	1.60	1.14	0.86	0.93
Large V-notch	1.67	1.08	1.29	1.07
Small V-notch	1.84	1.21	0.77	1.21

Both forms of test arrange the four materials in the same order, whatever form of test-piece is used.

The Charpy test has one practical advantage in that with paper board a much smaller proportion of notched specimens crack or break lengthwise instead of breaking through, thus making it easier to define the energy of fracture. This is illustrated by the figures in Table 14.

TABLE 14

		Total specimens tested	No. of specimens that crack without breaking through
Izod	Saw-cut notch	33	8
	Large V-notch	48	30
	Small V-notch	51	22
Charpy	Saw-cut notch	32	6
	Large V-notch	35	0
	Small V-notch	35	1

Accuracy of results

In considering the relative accuracies of the various forms of test, a clear distinction must be made between the following sources of error:

Variability errors, due to the nonuniformity of the material and imperfections in the test-pieces. These are the same for both types of machine.

Machine errors, e.g., energy losses due to friction and windage (where not accurately known and allowed for), nonparallelism of the striking edge and the struck face of the specimen, center of percussion not lying in the striking edge, lack of rigidity of specimen holders, and the like.

Flying-fragment errors, due to energy imparted to detached pieces of the specimen by the pendulum after it has broken the specimen. This error does not arise in the falling-weight test.

Nonmeasurement error, due to the absence of an actual measurement of the impact strength of each specimen in the falling-weight test.

Pendulum machine.—The values of impact strength obtained with this machine are affected by variability, machine, and flying-fragment errors. The following considerations therefore apply to the sum of these errors.

In examining the pendulum test results, the first step was to calculate the standard deviation. In calculating these values all the results in which a

complete break was obtained have been included, irrespective of whether the excess energy was greater or less than 25 per cent. It is obviously illogical to disregard results where the excess energy is greater than 25 per cent, because this practically amounts to excluding the weakest specimens.

Where a specimen failed to break or did not break through completely, the result cannot be used in calculating the standard deviation, and in these cases the results are given in brackets.

The standard deviation (D) has been used to calculate the standard error (SE) of the mean, using the formula $SE = D/\sqrt{N}$ where N is the number of individual results. As the number of results used in calculating the standard deviation varies between 10 and 14 in the different tests, the standard error has been calculated for a uniform number of 10 specimens, so as to give a true basis for comparing the different materials and test-pieces. For the same reason the standard error is given also as a percentage of the mean value of impact strength for all the specimens used in calculating the error (see Table 15).

TABLE 15

	Fabric board			Paper board			Bakelite			Ebonite		
	D	SE	$SE\%$	D	SE	$SE\%$	D	SE	$SE\%$	D	SE	$SE\%$
Unnotched	5.3	1.8	2.5	(1.7)	(0.55)	(4.5)	(0.78)	(0.25)	(3.4)	2.3	0.75	4.3
Saw-cut notch	(5.6)	(1.8)	(3.9)	0.63	0.21	3.1	0.23	0.07	3.3	0.41	0.13	3.8
Large V-notch	(4.2)	(1.3)	(2.8)	0.22	0.07	1.2	(0.25)	(0.07)	(3.4)	0.26	0.09	2.5
Small V-notch	(2.8)	(0.95)	(2.2)	0.55	0.18	2.7	0.14	0.04	2.1	0.20	0.06	2.1

D = standard deviation, kg. cm. per sq. cm.

SE = error of mean for 10 specimens, kg. cm. per sq. cm.

$SE\%$ = error of mean for 10 specimens, as percentage of the mean.

Judging by the percentage standard error, there is not much difference in general between the accuracy of the results given by the four forms of test-piece, though there is a tendency for the V-notched specimens to give rather better results than the others.

Falling-weight machine.—The values for impact strength obtained with this machine by the method used in the present work are affected by the variability, machine, and nonmeasurement errors. The magnitude of these combined errors cannot be deduced directly from the experimental results because a value for impact strength is not obtained with each specimen.

The standard error of the percentage of breaks obtained with any given number of specimens subjected to the same blow can be calculated if it is known what percentage of breaks this blow would produce with a very large number of specimens (this is worked out in Appendix II for the case of 50 per cent breaks). The standard error of the impact strength deduced by plotting the experimentally observed percentage of breaks against the blow, however, is difficult to estimate from the errors for the individual points on the graph, because the position of the curve at 50 per cent break (which determines the value deduced for impact strength) is influenced more by those points near the middle of the curve than by those near its ends.

An approximate value for the standard deviation due to variability plus machine errors can be obtained from the curve of percentage breaks (plotted vertically) against energy of blow, by measuring the slope of this curve at its steepest point, *i.e.*, corresponding to 50 per cent breaks. In an ideal curve of this type this slope is $100/D\sqrt{2\pi}$ (see Appendix II). The values of D calculated by this formula from the slope are compared, in Table 16, with those for

TABLE 16
STANDARD DEVIATION (PERCENTAGE)

	Fabric board			Paper board			Bakelite			Ebonite		
	P	FI	FC	P	FI	FC	P	FI	FC	P	FI	FC
Untouched	8	3	2	14*	10	12	10	3	1	14	3	6
Saw-cut notch	12	5	4	10	9	6	9	7	6	12	11	13
Large V-notch	9	7	7	4	14	5	11	6	2	8	12	3
Small V-notch	7	9	7	9	7	5	6	5	7	6	5	7
Mean	9	6	5	9	10	7	9	5½	4	10	8	7

P = Pendulum.
FI = Falling-weight Izod test.
FC = Falling-weight Charpy test.

* 11 for the 7 specimens (out of a total of 15) giving less than 25 per cent excess energy.

the pendulum test (from Table 15). For convenience of comparison all the figures are given as percentage of the mean value of impact strength for all the specimens used in calculating the standard deviation.

No great accuracy can be claimed for the individual figures, but the means for four types of test-pieces may be accepted as giving some idea of the relative accuracies of the different forms of test. This average does not vary greatly from one form of test to another, except with fabric board and Bakelite. Taking a grand average for each test gives the following figures: pendulum (Izod), 9.2 per cent; falling weight, Izod, 7.4 per cent; falling weight, Charpy, 5.8 per cent.

The higher value for the pendulum machine, unless due to flying-fragment errors, would indicate that the machine errors are greater than in the falling-weight machine, since the variability error must be the same with both. The apparent advantage of the Charpy over the Izod test on the falling-weight machine may be connected with the fact that the former involves a heavier blow (see Table 11), so errors due to windage and friction tend to be less serious.

The above figures are not proportional to the standard errors of the final results obtained from a given number of specimens with the pendulum and falling-weight machines, respectively, because the figures for the latter do not include the nonmeasurement error. (This is evident when it is considered that this error does not affect the slope of the percentage breaks/energy of blow curve, but only the accuracy with which this slope can be determined.) The magnitude of this error cannot be determined exactly, but a rough idea can be obtained from the fact that it is about 75 per cent of the variability error (see Appendix II). If it is assumed, as seems reasonable, that the variability error represents a considerable proportion of the errors considered above (Table 16 *et seq.*), the values for the falling weight machine would thus have to be multiplied by about 1.25 (i.e., $\sqrt{1^2 + 0.75^2}$) to include the nonmeasurement error. It may therefore be concluded that, as far as the present results can indicate, there is little to choose, as regards the accuracy of the final results from a given number of specimens, between the pendulum machine used by the excess energy method and the falling-weight machine giving merely a "break" or "no-break" result. This conclusion, of course, applies only to the particular machines used in these tests. The larger number of specimens used with the falling-weight machine should, however, give this machine the advantage.

The figures in Table 16 indicate that there is no great difference between the average standard deviations for the four types of test-piece: unnotched, 7.2; saw-cut notch, 8.6; large V-notch, 7.3; small V-notch, 6.7.

Excess energy in pendulum tests

In examining the pendulum test results to see whether the measured impact strength is influenced by the amount of excess energy in the pendulum, it is clear that no information can be obtained from a set of results obtained with the same initial energy in the pendulum, because the excess energy varies solely in accordance with the strength of the specimen, being low when this is high and *vice versa*.

It is, therefore, necessary to compare the mean impact strengths obtained with different blows. In the present experiments this can be done in all cases except Bakelite and ebonite with large V-notches and Bakelite with the small V-notch (see Table 17).

TABLE 17

	Fabric board			Paper board		
	No. of specimens	Blow	Impact strength	No. of specimens	Blow	Impact strength
Unnotched	8	130	71.4	4	24.6	13.5
	4	148	65.5	9	27.9	11.15*
				2	29.0	16.3
Saw-cut notch	3	69.3	43.3	3	9.36	6.18
	3	72.3	46.6	9	10.76	6.68
	7	75.5	44.9			
Large V-notch	6	69.0	46.2	10	9.36	6.32
	5	72.4	43.2	1	10.76	5.82
	2	75.5	45.0			
Small V-notch	9	61.2	40.7	9	9.36	6.41
	3	68.5	39.1	2	10.76	6.17
	Bakelite			Ebonite		
	No. of specimens	Blow	Impact strength	No. of specimens	Blow	Impact strength
Unnotched	4	12.3	6.82	2	27.9	13.8
	4	14.1	7.52	10	33.5	17.4
	2	15.5	8.45			
Saw-cut notch	8	3.49	2.28	1	5.09	3.50
	2	4.4	2.52	11	5.58	3.29
	2	5.3	2.80	2	6.49	3.56
Small V-notch	—	—	—	8	5.09	3.18
				2	5.58	3.24

NOTE.—Where two or three nearly equal blows were used, with only one or two specimens at each, the results have been averaged. Values for blow and impact strength are in kg. cm. per sq. cm. All results refer to specimens that broke completely through.

* This value was obtained with the heavy pendulum and the other two with the small pendulum.

The number of specimens in each group is unfortunately too small in many cases to enable much reliance to be placed on differences between the impact strengths obtained with the different blows. The only case in which there appears to be a progressive change in measured impact strength with variation of the blow is Bakelite, where both unnotched and saw-notched specimens give higher values the heavier the blow.

Assuming for the moment that the measurement of impact strength is influenced by the magnitude of the blow, it is necessary to consider the question of fixing a maximum limit for excess energy. The excess that must logically be

permitted depends on the variability of the material. If the weakest specimen has an impact strength x per cent lower than the strongest specimen, the excess energy limit cannot reasonably be fixed at less than x per cent because if a smaller limit is fixed and the blow adjusted so that this is never exceeded, the strongest specimens will not be broken and will therefore be disregarded, whereas if the blow is increased so as to break these the excess energy will exceed the limit with the weakest specimens, which will then be disregarded. In either case, therefore, the specimens showing extreme values of impact strength will be excluded and a false mean obtained.

The percentage difference between highest and lowest values, *i.e.*, x , as defined above, is given in Table 18 for each set of tests. In some cases the

TABLE 18
DIFFERENCE BETWEEN HIGHEST AND LOWEST (AS PERCENTAGE OF HIGHEST)

	Fabric board		Paper board		Bakelite		Ebonite	
Unnotched	25	(14)	43	(27)	25*	(25)*	35	(35)
Saw-cut notch	36*	(27)	25	(24)	24	(11)	31	(29)
Large V-notch	27	(27)	11	(8)	31*	(31)*	22	(22)
Small V-notch	22	(22)	31	(19)	21	(21)	16	(16)

* Minimum figure, because the highest value was for a specimen that did not break completely through.

highest or lowest value was obtained with a heavier or lighter blow than most of the values. To eliminate any possible influence of variation of the blow, figures are given also (in brackets) for the maximum variation among results obtained with the same blow.

Taking the figures relating to all the specimens, the variation is greater than or equal to 25 per cent in ten cases out of sixteen and even if attention is confined to results obtained with a constant blow the 25 per cent limit is reached or exceeded in seven cases. Moreover, these cases occur with all four materials and with all types of test-piece, so that it would appear impossible to adhere to the 25 per cent maximum excess energy limit if a true mean value is to be obtained.

ADVANTAGES AND DISADVANTAGES OF THE TWO TYPES OF MACHINE

The pendulum type of machine appears to have the following inherent advantages over the falling-weight type:

(1) An actual value is obtained for the strength of each specimen, so that the variability of the material and the probable error of the mean value are more readily investigated than with the falling-weight machine. However, this applies only to the measurement of the energy required for a complete break. For practical purposes the smallest energy that cracks or otherwise damages the specimen is of primary interest, and this is determined just as easily by the falling weight as by the pendulum.

(2) The fact that a value is measured for each specimen eliminates the non-measurement error (see Section IV (c) (ii)) that enters into the result from the falling-weight machine.

(3) Friction and windage corrections can be determined, so that even though these determinations may not be very accurate, there is an advantage over the falling-weight machine where such corrections cannot readily be determined.

On the other hand the pendulum machine has the following disadvantages:

(1) It requires some care in designing the machine to locate the center of percussion exactly on the striking edge, especially when the load has to be varied.

(2) The fact that the blow is struck horizontally necessitates the machine being very rigid and firmly fixed to a rigid foundation when heavy blows are used. With the vertical blow delivered by the falling-weight machine this is not necessary.

(3) It is not so easy to provide for both Izod and Charpy tests as on the falling-weight machine, since a different set of pendulums must be provided in addition to the Charpy form of specimen support.

Another disadvantage was noticed in using the pendulum machine designed for this investigation, though it is not necessarily inherent in this type of machine. With the light pendulum an excess energy was often recorded when the blow did not damage the specimen in any way. This may be due to the fact that this pendulum consists of two wires lying in a plane perpendicular to the direction of motion, so if the specimen does not break, the wires may bend forward slightly at the moment of impact. If this occurs, the arm that actuates the pointer strikes the latter and causes it to move some distance (depending on its frictional resistance), thus registering an apparent excess energy. Moreover, in tests where the excess energy was very small, the excess recorded by the pointer was noticeably greater than that indicated by the swing of the pendulum after breaking the specimen. This discrepancy was noticed only with excess energies less than about 10 per cent.

In this type of machine it is clearly necessary to ensure that the pointer on the excess energy scale cannot be caused to move further than the pendulum itself. Since this investigation was carried out, this source of error has been eliminated by redesigning the light pendulum.

SUMMARY

A comparison has been made of impact tests by the pendulum machine (Izod) and by the falling-weight machine (Izod and Charpy), using fabric board, paper board, molded resin (Bakelite), and ebonite, each in four types of test-pieces; unnotched, saw-cut notch, V-notch with 1 mm. root radius, and V-notch with 0.5 mm. root radius.

The effect of notching on impact strength varies from one material to another, and may alter their order of merit. Saw-cut and V-notches with the same root radius nearly always give about the same results, and reducing the root radius usually (but not always) reduces the impact strength.

The pendulum machine always gives higher results than the falling weight-machine in Izod tests, and the ratio varies with the material, though not sufficiently to alter the order of merit.

Under the conditions used in the present tests with the falling-weight machine, Charpy tests (70 mm. between supports) nearly always give higher values than Izod tests (22 mm. striking distance), but both arrange the materials in the same order of merit.

Standard errors are worked out for the pendulum test results; V-notched specimens appear to give, if anything, the best accuracy.

The sources of variability in test results, and hence of errors in the final value, are discussed in an attempt to compare the accuracies of the two ma-

chines. Although an exact comparison could not be made, there appears to be no great difference between the two machines as regards the accuracy of the result obtained with a given number of test-pieces. The four types of test-piece differ very little, on the whole, in this respect.

With the falling-weight machine, the Charpy test appears to give rather better accuracy than the Izod test.

There is no definite evidence that the amount of excess energy in the pendulum test influences the result, except perhaps with Bakelite.

The variability of all four materials tested is such that a maximum excess energy limit of 25 per cent cannot be adhered to without excluding either the weakest or the strongest specimens and so obtaining a false mean.

In Izod tests on the pendulum machine a 20 mm. striking distance gives higher values for fabric board than a 35 mm. striking distance; the former has the advantage that no incomplete breaks occur, as happens with the longer striking distance.

Attention is drawn to certain advantages and disadvantages of the two types of machine, and to the necessity for defining a "break" in the case of laminated materials, where cracks or incomplete breaks are frequent.

APPENDIX I

THEORY OF THE PENDULUM TEST

Let:

- E_1 = potential energy of pendulum before release.
- E_2 = kinetic energy of pendulum at moment of impact.
- E_b = energy required to break specimen.
- x = percentage excess energy reading obtained by allowing pendulum to swing without a specimen in position and with pointer initially set at zero.
- y = percentage excess energy reading obtained by allowing pendulum to swing several times from the release position after taking the x reading and without readjusting pointer. y is greater than x because these later swings do not encounter resistance in moving the pointer from zero.
- z = percentage excess energy reading after breaking specimen (pointer initially at zero).
- E_x, E_y, E_z = potential energies of pendulum at positions corresponding to readings of x, y, z on percentage excess energy scale.
- e = fraction of energy lost by windage and friction in bearings.
- f = fraction of energy lost by windage, friction in bearings, and in moving pointer.
(e and f are assumed independent of angle of swing.)

Then $E_2 = (1 - e)E_1$ and since the y reading does not involve friction of pointer mechanism:

$$E_y = (1 - e)E_2 = (1 - e)^2 E_1$$

But $E_y = yE_1/100$, hence

$$1 - e = \sqrt{y}/10. \quad (1)$$

As the x reading involves friction of pointer mechanism:

$$E_x = (1 - f)E_2 = (1 - f)(1 - e)E_1$$

But $E_x = xE_1/100$, hence $(1 - f)(1 - e) = x/100$;

whence from (1):

$$(1 - f) = x/10\sqrt{y} \quad (2)$$

Now:

$$E_s = (1 - f)(E_2 - E_b),$$

whence

$$E_b = E_2 - E_s/(1 - f).$$

But:

$$E_s = zE_1/100;$$

therefore from (2):

$$E_b = E_1\sqrt{y}/10(1 - z/x) \quad (3)$$

APPENDIX II

COMPARISON OF ERRORS OF PENDULUM AND FALLING-WEIGHT METHODS

It is estimated that the energy of fracture can be measured on the pendulum machine with an accuracy of about 0.5 per cent. The blow given to the specimen in the falling-weight machine can be measured with a similar degree of accuracy, exclusive of the errors due to windage and friction, which cannot easily be estimated. One of the principal factors which determines the accuracy of the mean result is, therefore, the variability of the material under test combined with the nonmeasurement error in the case of the falling-weight machine.

An attempt has been made to estimate the errors of results obtained by the two methods of testing, assuming the material to be one whose impact strength obeys the normal law of chance distribution.

Falling-weight machine

Suppose tests to be made with a blow that would break 50 per cent of a large number of specimens. In any test on a single specimen the result (percentage breaks) must obviously be either 0 or 100, and since the mean for a large number of specimens is 50, the standard deviation of individual results from the mean must be 50. The standard error of the percentage breaks determined by tests on n specimens must, therefore, be $50/\sqrt{n}$.

Consider now the curve obtained by plotting percentage breaks (y) against energy of blow (x) for a large number of specimens. The slope of this curve (dy/dx), for any value of x , equals the ordinate, for the same value of x , of the frequency-distribution curve of impact strength for the material under test. In the present case this curve is assumed to be the normal probability curve corresponding to a standard deviation D . When x equals the mean impact strength of the material the ordinate of this curve is $N/D\sqrt{2\pi}$ (N = number of specimens), whence $dy/dx = N/D\sqrt{2\pi}$, or in the present case, since $N = 100$ when breaks are plotted on a percentage scale:

$$dy/dx = 100/D\sqrt{2\pi} \quad (1)$$

As shown above, the standard error of a single determination of y with n specimens, when y is about 50, equals $50/\sqrt{n}$. The standard error of the corresponding value of x is therefore $50/\sqrt{n}$ divided by dy/dx , that is $D\sqrt{\pi/2n}$ (from (1)).

Let m determinations of y be made, each with n specimens and with a blow in the neighborhood of the mean impact strength, so the standard error of y is

approximately constant, and let the values of y be plotted against the corresponding value of x and a smooth curve be fitted through the m points so obtained. Then the standard error (S) of the measured impact strength (*i.e.*, the value of x corresponding to $y = 50$, as read from the curve) is:

$$S = D\sqrt{\pi/2nm} = D\sqrt{\pi/2M} \quad (2)$$

where M = total number of specimens tested ($=nm$).

It can be shown in an analogous manner that, with a blow giving either 25 or 75 per cent breaks with a large number of specimens, the standard error of the result is rather greater than that given by Formula (2).

It is evident, therefore, that under the best conditions, *i.e.*, where all the blows are close to the mean impact strength of the material, the standard error of the measured value of impact strength is about $\sqrt{\pi/2M}$ times the standard deviation characteristic of the material.

Pendulum machine

The standard error of the mean result obtained with M specimens is D/\sqrt{M} .

Excluding machine errors and flying-fragment errors, therefore, the standard error for the falling-weight machine used under the best conditions (Formula (2)) is $\sqrt{\pi/2}$ ($= 1.26$) times the error for the pendulum test using the same number of specimens. The nonmeasurement error, *i.e.*, the error arising from the failure of the falling-weight test to measure the strength of each specimen, is thus 77 per cent, *i.e.*, $100 \times \sqrt{1.26^2 - 1^2}$ or perhaps more, of the variability error characteristic of the material.

Values of the standard error calculated by the above formulae are given below for ten specimens (as used in the pendulum tests) and 32 specimens (the average number used in the falling weight tests):

No. of specimens	Pendulum	Falling weight
10	0.316D	0.396D
32	0.177D	0.222D

Under the conditions of testing used in the present experiments, therefore, the falling-weight machine should give a more accurate final result than the pendulum (neglecting errors due to the machine itself and to flying fragments), but this is due solely to the use of a larger number of specimens with the former.

REFERENCES

- ¹ Church and Daynes, *Trans. Inst. Rubber Ind.* **13**, 96 (1937); *RUBBER CHEM. TECH.* **11**, 224 (1938).
- ² In accordance with the decision made at the Second E.R.A. Conference on Impact Testing.

ELASTICITY MEASUREMENTS ON POLYCHLOROPRENES *

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During the last fifteen years great interest has been directed toward the physicochemical behavior of synthetic high-molecular compounds; this is perhaps especially true of rubberlike materials. The main problem here is to get a proper understanding of the factors which determine the specific property of high elasticity. Many investigations have appeared in this field, and a short review of the modern theories is given below. It seems, however, that comparatively little attention has been devoted to the influence of the different sizes of the macromolecules on the network structure in the polymer and to the extent to which the molecular weight determines the elastic properties. The purpose of this paper is to give a brief account of some preliminary attempts to study the building up of network structures by means of molecular-weight determinations, and especially to establish the relation between the size of the macromolecules in solution and the constants characterizing the network structure.

The most fundamental difference between the elastic properties of ordinary solid bodies such as metals and of rubberlike materials is that, on isothermal stretching at constant volume, the change in entropy is zero for solids, whereas the change in internal energy is zero for rubbers. This means that in solids the stress causes a deformation of the molecular structure in such a manner that the ordered state is not disturbed. In rubberlike materials there is no deformation of chemical bonds or valence angles, but only a rearrangement of the segments in the molecular chains as a result of free rotation about single carbon-carbon bonds. It must, however, be emphasized that these conditions, *i.e.*:

$$(\partial \Delta S / \partial \Delta l)_T = 0 \quad \text{and} \quad (\partial \Delta E / \partial \Delta l)_T = 0$$

(S = entropy, E = internal energy, l = length of specimen, and T = absolute temperature) are valid only for ideal substances. In real matter the changes in free energy are due to changes both in entropy and in internal energy.

It is a well-known fact that high-molecular compounds with thread-shaped molecules crystallize when they are stretched to high elongations. According to the ability of the macromolecules to fit into a crystal lattice, the ordered state can be more or less pronounced. Mark¹ has pointed out that the free energy can have its absolute minimum either in the initial unstretched state or in the final arrangement of the system in the stretched state. The main factors influencing the position of the minimum are the molecular attraction between the chains, the temperature, other external forces, and the above-mentioned ability of fitting geometrically into a lattice. The initial state can be assumed to consist of curled-up chains, and represents in the case of large intramolecular forces

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a stable state. The final arrangement is determined by the mutual attraction between adjacent chains caused by intermolecular forces. If these forces are small, we have a condition typical of rubberlike materials. The chains have a tendency to return to their original states.

The stretching of such a material involves first of all a breaking down of the internal crystallization. The molecules are brought into a more probable position and, depending on the strength of the intramolecular forces, the gain in entropy is small or large in comparison with the loss in potential energy. The relative values of entropy and internal energy depend on the substance in question. Evidently one must always bear in mind that, at the start of the stretching of a rubber specimen, a certain part of the force exerted is used up in breaking down certain bonds (hydrogen bonds) between chain segments.

The gain in entropy on stretching was first calculated by Kuhn³, Wall³, and Guth and Mark⁴. The calculations are based on a statistical study of the possible configurations of the chain molecules. The probability $p(x, y, z)$ of the molecular chain having components of length x, y, z , respectively, along each of the three coördinate axes is:

$$p(x, y, z) dx dy dz = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(x^2+y^2+z^2)} dx dy dz. \quad (1)$$

where

$$\frac{1}{\beta^2} = \frac{2}{3} \cdot l_c^2 \cdot Z \frac{1 + \cos \theta}{1 - \cos \theta} \quad (2)$$

Here l_c is the carbon-carbon bond distance, Z the number of links in the chain, and $180^\circ - \theta$ the valence angle. Using the assumptions⁵ that all molecules have the same chain length, that the extension of the length components of each molecule changes in the same ratio as the components of length of the macroscopic rubber, and that the volume of the rubber remains unchanged, Wall obtains from formula 1 the following expression for the change in entropy:

$$\Delta S = -\frac{1}{2} N_0 k \left(\alpha^2 + \frac{2}{\alpha} - 3 \right) \quad (3)$$

where N_0 is the number of molecules, k is Boltzmann's constant, and $\alpha = 1 + \gamma$, where γ equals the fractional extension. Now the following thermodynamical relationship is valid in the case of reversible stretching:

$$\kappa = (\partial \Delta E / \partial \Delta l)_T - T(\partial \Delta S / \partial \Delta l)_T \quad (4)$$

It is the force κ which keeps the rubber specimen in the stretched state. Observing that $\gamma = \Delta l / l_0$ (l_0 = original length) one obtains from Equations 3 and 4:

$$\kappa = (\partial \Delta E / \partial \Delta l)_T + N k T (\alpha - 1 / \alpha^2) \quad (5)$$

or, since $Nk = R\rho/M$:

$$\kappa = (\partial \Delta E / \partial \Delta l)_T + \frac{RT\rho}{M} (\alpha - 1 / \alpha^2) \quad (5')$$

The force κ refers to the original cross-section, N is the number of molecules per cm.³, ρ is the density of rubber, and M is the molecular weight. The expression $(\partial \Delta E / \partial \Delta l)_T$ represents the part of the force exerted which causes changes in internal structure, i.e., deformation of bonds and valence angles. To get a complete description of the stress-strain curves it would be necessary

to make certain assumptions about the nature and magnitude of the forces which cause these deformations.

Flory and Rehner⁶ have carried out a statistical treatment on a three-dimensional network model, and have succeeded entirely in avoiding the assumption of Kuhn and Wall regarding the manner in which the chain-length distribution is transformed by macroscopic deformation of the rubber sample. The expression for ΔS is quite the same as Equation 3, but in this case M in Equation 5' must be the molecular weight of the part of the macromolecule between two points of cross-linkage, *i.e.*, an average molecular weight of an elastic unit. Using the cross-linked network model, Flory and Rehner⁷ have also studied the swelling of rubber and obtain, in the case of swelling equilibrium with a pure solvent, the following expression for the molecular weight:

$$M_e = \frac{\rho V_1 v_2^{\frac{1}{3}}}{K v_2^2 / 2 + \ln(1 - v_2) + v_2} \quad (6)$$

where ρ is the density of rubber, V_1 the molar volume of the solvent, v_2 the volume fraction of polymer in the swollen gel, and K a quantity which depends on the heat of mixing. Thus it is possible to obtain values of M in two different ways, according as the process is stretching or swelling.

Huggins⁸ has recently developed a theory of rubber elasticity which is based on hypothetical model substances consisting of a large number of like systems, each being in equilibrium between two states with different arrangements of the atoms. He obtains rather complicated expressions for the stress-strain dependence. The discussions in this paper have hitherto been based only on Relation 5'. But at higher elongations especially, Huggins' treatment seems to be preferable.

As to the influence of molecular weight, *i.e.*, the length of the macromolecules, on the elastic properties, Mark⁹ points out that the material must have a certain degree of polymerization and that this minimum degree depends on the substance. Thus, for polyhydrocarbons the tenacity below a polymerization degree of 80 is negligible. Above 80 it increases roughly proportionally to the chain length, and at about 250 the curves begin to flatten out. First at polymerization degrees of about 700 the tenacity no longer depends on the chain length. The shape of the distribution curve also influences the mechanical properties. Small amounts of low-molecular-weight materials (polymerization degree below 150) have an especially detrimental effect, and it is therefore necessary to have a comparatively low degree of polydispersity.

Another important question is the branching and cross-linking of the chains. It has not been possible to make any clear-cut decision on this problem, but a low degree of branching probably has very little effect on mechanical properties. Highly branched chains and cross-linked molecules, on the other hand, give a very hard and stiff material. The very few measurements in this field do not tell us much about the real network structure and how molecules with different chain lengths build up the network. It is therefore of interest to obtain experimental data on a range of synthetic materials with different molecular weights, and to follow the change in elasticity from the unvulcanized to the vulcanized state.

To obtain stress-strain curves for the rubber samples, a Polanyi dynamometer¹⁰ was constructed. Meyer and Ferri¹¹ have used a similar apparatus. The main features of the dynamometer are seen in Figure 1. Two arms A and B (with a framework) are movable on a steel rod D. During the measurements A is fixed and B moved downwards or upwards by means of a screw F

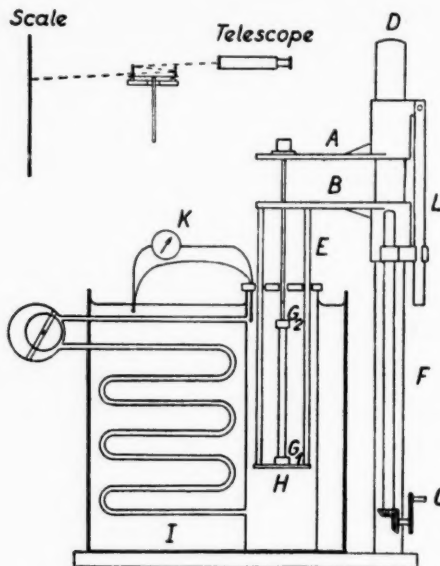


FIG. 1.—Dynamometer for elasticity measurements (Polanyi).

and a handle C, causing the rubber specimen between the clamps G_1 and G_2 to stretch or unstretch. On A a steel spring rests on two steel knife edges. At each end the spring carries a small mirror, and as the spring bends these mirrors incline towards each other. The bending of the spring depends on the tension set up in the specimen, and by observing an illuminated scale at a distance of about 2 m. from the apparatus through a telescope, it is possible to follow the displacement of the scale image. By calibrating the scale in force units, one can thus obtain the total force exerted on the spring. The initial and actual lengths of the specimen can be read off on a scale L (a cathetometer has recently been constructed for the length measurements and this is an obvious improvement). The stretching occurs in an air thermostat (H), and the air is heated by means of a coil (I) immersed in a water thermostat. A positive displacement pump effects the circulation. The temperature in H is measured by means of a thermocouple and a galvanometer (K). During the measurements the specimen can be observed through glass windows in the thermostats.

As shown by Meyer¹², it is possible with this apparatus to calculate the quantities ΔE and ΔS from the stress-temperature curves. Such measurements have not yet been made. Only in a few cases has the relation between stress and temperature been investigated.

The following rubber samples were used: *Sample I*: unvulcanized polychloroprene from homogeneous polymerization; molecular weight from sedimentation and diffusion in chloroform about 130,000. *Sample II*: unvulcanized polychloroprene (Neoprene-E); molecular weight from sedimentation and diffusion in chloroform about 204,000. *Sample III*: unvulcanized polychloroprene from emulsion polymerization; as the sample was soluble in chloroform only up to 32 per cent, the molecular weight was not determined; the sample contained 2 per cent of sulfur. *Sample IV*: vulcanized rubber; this sample was only used to compare the unvulcanized and vulcanized states.

The molecular weights for I and II were taken from an investigation of a large number of different polychloroprenes carried out by I. Svedberg and the author¹³.

From Samples I and II rubber specimens were prepared according to Treloar¹⁴, except that the samples were dissolved in chloroform. The thickness of the films was about 0.5 mm. Samples III and IV were in the form of thin sheets. In measuring the stress it was necessary to let such a long time elapse that the relaxation process had time to end completely. After 15–20 minutes the stress was constant within a few tenths of one per cent.

As samples I–III were unvulcanized, it was not to be expected that the stretching procedure would be reversible in a thermodynamic sense. The hysteresis losses were very large too, as is seen from Table 1 containing the

TABLE 1
HYSTERESIS LOSSES FOR POLYCHLOROPRENES

Sample	Temperature (°C)	Relative elongation (per cent)	Hysteresis losses (per cent)
II { first cycle second cycle third cycle	20.0	2.07	75.5
	20.0	2.07	37.4
	20.0	2.07	34.5
III first cycle	29.2	4.37	35.9
	31.2	4.89	40.5
	34.5	4.54	29.3
	37.4	4.57	26.7
	39.8	4.51	20.3

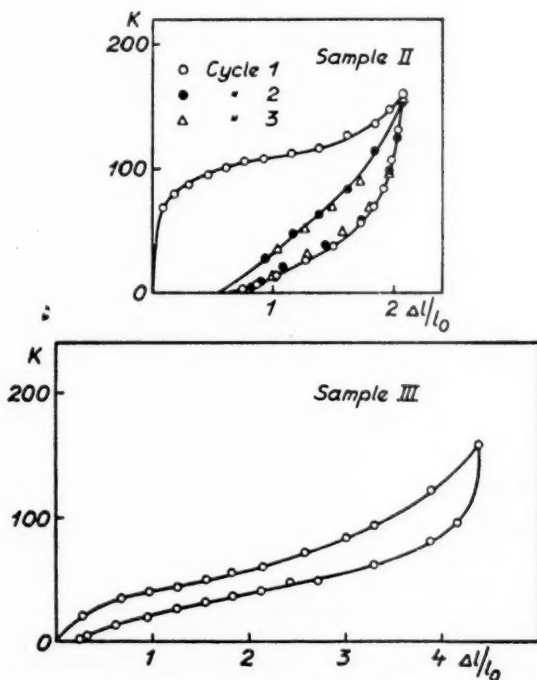


FIG. 2.—Stress-strain curves and hysteresis cycles for Samples II and III. κ is the force in grams per millimeter

values for Samples II (different cycles) and III (different temperatures). The shapes of the curves for Sample II and Sample III (29.2° C) are shown in Figure 2. The similarity between the curves for Sample II and those obtained by Bostroem¹⁵ for raw rubber (smooth sheets) is obvious, and it can, therefore, be assumed that even in the case of polychloroprene the large hysteresis loss for the first cycle is due to a structure which is broken down when the rubber is first extended. The curve for Sample III is not so steep at low elongations, and is in this respect more similar to that of vulcanized rubber. From this and the smaller values for the hysteresis losses, the conclusion can be drawn that the addition of sulfur to the polymerization mixture causes a slight vulcanization or, in other words, a more networklike structure. As can be expected, the hysteresis losses decrease with increasing temperature.

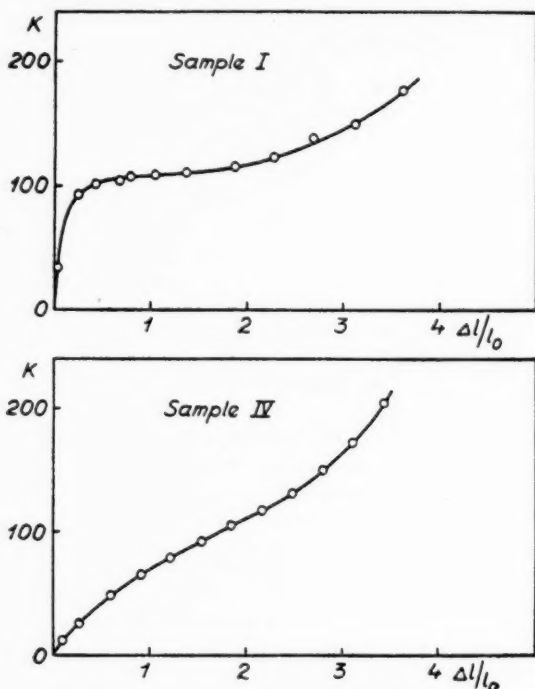


FIG. 3.—Stress-strain curves for Samples I and IV.

The stress-strain curves obtained for Samples I-IV are shown in Figures 2 and 3. The stress is referred to the original cross-section of the specimen. Especially for unvulcanized rubber it is difficult to reproduce the curves. If the measurements are carried out on specimens of different sizes, the stress changes within 10 per cent. For vulcanized rubber the reproducibility is fairly good. Starting from these curves Formula 5' has been used to get values of M . The expression $(\partial \Delta E / \partial \Delta l)_T$ has been assumed to be a constant, and is also calculated under this assumption. Evidently this is only a very cured approximation, especially for the first and last parts of the curves, as is seen from Figure 4, where the stress has been plotted vs. the expression $\alpha - 1/\alpha^2$ for Samples I and IV and the straight lines correspond to Formula 5'. It

must be emphasized that on the whole it is incorrect to use this formula, if the constants are to express changes in thermodynamic quantities for a reversible process. Yet it is suitable to use such an equation, which is based on certain assumptions about internal network structure, to characterize the elastic nature of the material, especially as it describes the behavior of vulcanized rubber fairly well up to rather high elongations (*cf.* Figure 4). The values obtained are given in Table 2.

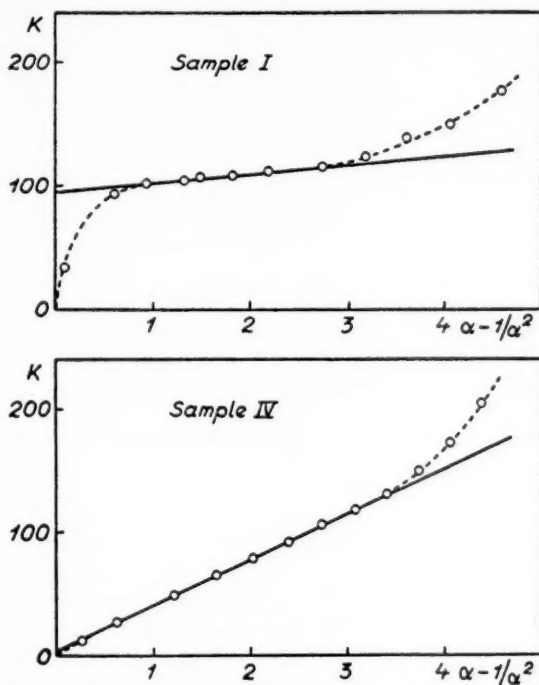


FIG. 4.—The force κ plotted against $\alpha - 1/\alpha^2$ for Samples I and IV.

TABLE 2
VALUES OF $(\partial\Delta E/\partial\Delta l)_T$ AND M ACCORDING TO FORMULA 5'

Sample	Temperature (°C)	$(\mu\Delta E/\mu\Delta l)_T$ (g.-cm./cm. ²)	M
I	25.0	8520	42,200
	25.0	7860	35,200
	25.0	9520	44,200
		8630	40,500
II	20.0	8400	21,000
III	29.2	1430	22,100
	31.2	1470	16,500
	34.5	2000	24,300
	37.4	1690	27,800
	39.8	1810	33,200
	43.0	1930	41,400
IV	25.0	350	8,500

The expression $(\partial\Delta E/\partial\Delta l)_T$ cannot, as just pointed out, be constant for the whole curve. As the curves for Samples I and II are very steep at low elongations, the modulus is very high. The values 11×10^7 dynes per sq. cm. and 10×10^7 dynes per sq. cm., respectively, are calculated and are, compared to Sample III (0.7×10^7 dynes per sq. cm.), of another magnitude. Thus it can be assumed that, in certain points of the material, crystallization has occurred. This crystallization must be less pronounced the more the rubber is vulcanized; furthermore it probably depends on time. This follows from Figure 2, where the curves corresponding to the second and third time loading of the specimen do not exhibit any steep behavior. The values of $(\partial\Delta E/\partial\Delta l)_T$ determined from Equation 5' in the manner shown above can to some extent illustrate the degree of initial crystallization. From the values for Sample III there seems to be some dependence on temperature, but this cannot be further discussed until more experiments have been carried out. It seems very unlikely that the degree of crystallization should increase with increasing temperature.

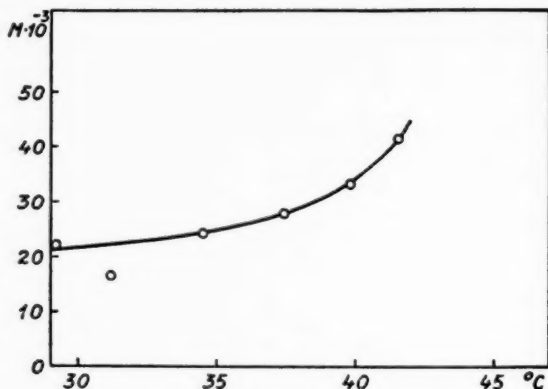


FIG. 5.— M as a function of temperature.

The values of M in Table 2 show an evident change from the unvulcanized to the more vulcanized state. It is interesting to see that Samples I and II, which have almost the same values of $(\partial\Delta E/\partial\Delta l)_T$, have such different values of M . If M is related to the part of the macromolecule between two points of cross-linkage, the number of those points are on an average per molecule for Sample I equal to 3 and for Sample II equal to 10. Sample II should consist of a more perfect network structure, compared to Sample I. As both samples are unvulcanized in the common sense, it is probable that Sample II has a larger content of μ -polymer. For Sample III, the values of M increase with the temperature; this may be an indication that the forces in a point of cross-linkage in this case are very weak and cannot withstand the increased heat motion of the molecular segments. Hence the length of the molecule between adjacent points of cross-linkage increases. This increase seems to be more pronounced at higher temperatures, as is seen from Figure 5.

For the determination of M , it is also possible to use Equation 6. Investigations in this direction are in progress.

Naturally it is very difficult to draw conclusions which are valid for the substances in question. Firstly, the expressions on which the conclusion is based give only an approximate description of the material in certain respects and do not account for such phenomena as plastic flow, etc. Secondly, the substances are not well defined as to the types of polymers. It seems, however, from the results obtained in this investigation that certain comparisons can be made between different substances, and that further work will show the possibilities of getting better knowledge of the factors determining the transition from the unvulcanized to the vulcanized state.

SUMMARY

A brief survey of modern opinion as to the nature of the rubberlike state in certain high polymers is given. The behavior of unvulcanized and vulcanized rubber samples has been investigated with a Polanyi dynamometer. By means of Wall's formula for entropy changes on stretching, certain constants characterizing the samples have been calculated. The use of these constants for comparison purposes has been discussed.

ACKNOWLEDGMENT

This investigation is a part of a fundamental research program on synthetic rubber carried out at the request of the Governmental Commission of Industry in Sweden and under the guidance of Professor The Svedberg.

The author wishes to express his sincere thanks to Professor The Svedberg for his very kind interest and for the many facilities put at the author's disposal.

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PERFORMANCE OF BUTYL INNER TUBES

INFLUENCE ON TIRE LIFE *

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Since the first scientific paper on Butyl rubber was presented¹, numerous publications² have described the properties and compounding technique of this polymer. Although Butyl has been referred to as a specialty rubber, it can also be used to replace natural rubber in many applications.

Butyl was found to be a remarkable barrier to the passage of gases³, including air. The polymer also deteriorated very little on aging and had excellent tear resistance. Because of these properties Butyl was first considered for inner tubes, and in this application Butyl has found its largest commercial acceptance. Automobile inner tubes were first made experimentally in September, 1940. With Butyl made in the Standard Oil pilot plant this experimental work continued until April, 1943, when the first government plant began producing Butyl commercially. From that time until the present Butyl has been used successfully to manufacture all types and sizes of inner tubes ranging from bicycle tubes of 1½-inch cross-section to earth-mover tubes of 24-inch cross-section.

Butyl tubes were first used by the United States Army for service in the European war theater in May, 1944. The following month Butyl was used in essential civilian trucks; but not until September, 1945, was sufficient Butyl available for civilian automobile tubes.

COMPOUNDING

Compounding studies carried out early in the development of Butyl tubes indicated that Butyl inner-tube recipes could not be built around the recipes formerly used with natural rubber. Because of several unique fundamental characteristics, Butyl requires special compounding and handling techniques.

Nerve.—Pure-gum Butyl has a higher immediate elastic recovery than broken-down smoked sheets. Premastication was found to be ineffective in reducing this nerve; therefore, it was necessary to resort entirely to compounding techniques to obtain processability. Since softeners have a rather limited value, the present practice requires a rather high pigment loading and the use of pigments which exert considerable deadening effect.

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Contrary to natural rubber and Buna-S practices, the incorporation of carbon black in a Butyl inner-tube recipe is primarily to improve processability. It is not employed as a means of developing increased tensile strength, although it does raise modulus and enhance tear resistance to a much greater extent than do other pigments.

Resistance to Oxidation and Mill Breakdown.—When properly stabilized, Butyl exhibits great resistance to oxidation and mechanical breakdown. Plasticity changes during milling operations depend only on the temperature attained by milling.

This constancy of plasticity should prove to be an advantage and should lead to more uniform day-to-day factory operation. Moreover, as a result of this property, Butyl compounds for factory use may be designed on the basis of filler and softener changes alone, without regard to processing changes, such as reworking cycles, periods of standing, etc., factors which had to be taken into account in the use of natural rubber.

Cold Flow.—In spite of its high nerve, Butyl flows to a greater extent than natural rubber in a prolonged period of time. In inner-tube manufacture this property results in fold marks or side-wall breakdown of tube sections if they are stored on trays for extended periods. The use of 20 parts of EPC black in a Butyl tube compound was found to minimize cold flow. The use of small quantities of Polyac at the beginning of the black master batching operation increases the viscosity of Butyl and thereby minimizes cold flow and improves bruise resistance. A consideration of these properties of Butyl led to the development of the basic recipe of Table I for use in the manufacture of Butyl tubes.

TABLE I
RECIPE FOR MANUFACTURE OF BUTYL TUBES

Butyl	100	Petrolatum	2
Zinc oxide	5	Sulfur	2
EPC black	20	Thiuram-type accelerator ^a	1
SRF black	30	Thiazole-type accelerator ^b	0.5
Paraffin	1		

^a Satisfactory thiuram accelerators include Ethyl Tuads, Methyl Tuads, Monex, Mono-Thiurad, Tetrone-A, Thionex, Thiurad, Thiuram-E, Thiuram-M, Tuex, and Ethyl Tuex.

^b Satisfactory thiazole accelerators include Captax, MBT, and Thiotax.

A mixture of EPC and SRF blacks is employed to minimize bruising and reduced cold flow. A total loading of 50 parts of black is used to reduce nerve and tends to overcome shortness. Paraffin and petrolatum are used as representative, fully saturated aliphatic softeners which exert a minimum effect on curing rate. High concentration of ultra-accelerator and an excess of sulfur are used to obtain a fast rate of curing.

PERFORMANCE

As soon as the manufacture of Butyl tubes made it possible, test fleet operations were begun for the Standard Oil Company of New Jersey in San Antonio, Texas, to allow a close study of the performance characteristics of Butyl inner tubes under carefully controlled conditions. Road tests had been going on elsewhere for some time. The individual rubber companies had tested Butyl tubes in their own test cars, as had the various government test fleets throughout the country. But the results presented in this paper are all gathered from data obtained on test cars operated for this company.

Test fleet operations were begun in January 1944, using Pontiac and Chrysler automobiles. These automobiles travel at the rate of 60 miles per hour, 24 hours per day, 6 days per week. In January 1945, fleet operations were expanded to include the testing of truck tubes.

GROWTH

When applied in a tire and inflated, an inner tube is expanded as much as 35 per cent over its original dimensions. On deflation the tube does not return to its original size; it remains slightly larger, the increase depending on the permanent set of the rubber in service. This increase in the size of the tube is commonly referred to as its growth. Growth in service is one of the limiting factors in the life of an inner tube. The longer a tube remains in service the greater its growth. When this growth becomes great enough to make it difficult to remount the tube in a new tire without buckles or wrinkles, the tube must be discarded. For a tube to exhibit good growth characteristics it must not only possess balanced original physical properties but must maintain this proper balance after aging, particularly after aging in service.

Compounding changes exert considerable influence on growth. Changes in type and amount of black and in type and amount of softener are of importance, as is the use of such materials as Polyac or polybutene. Original tube dimensions, state of cure, type of service, and tube design also play an important part. Basically, however, growth depends on the type of Butyl used. The use of fast-curing (high modulus) Butyl results in a tube of correspondingly lower growth, compared with low modulus Butyl, over the entire range of compounding changes^a.

Experimental work along this line was carried out by choosing two lots of Butyl; they were compounded (Table II) and cured 40 minutes at 307° F,

TABLE II
COMPOUNDS USED FOR GROWTH TESTS

	Standard evaluation compd.	Inner-tube compd.
Butyl	100	100
Zinc oxide	5	5
Stearic acid	3	1
EPC black	..	30
SRF black	50	20
Thiuram-type accelerator ^a	1	1
Thiazole-type accelerator ^b	0.5	0.5
Sulfur	2	2

^a See footnote a, Table I.

^b See footnote b, Table I.

according to the standard evaluation method. The moduli at 300 per cent elongation were as follows: Butyl for tube SO-2, 400 pounds per square inch; Butyl for tube SO-8A, 650 pounds per square inch. The two different lots of polymer were then compounded in the same tube recipe and cured into inner tubes (column 3, Table II).

Tube SO-2 (low-modulus Butyl) was compared with tube SO-8A (high-modulus Butyl) in a road service test. The results of this test are given in Figure 1, which demonstrates the lower growth of the high-modulus Butyl.

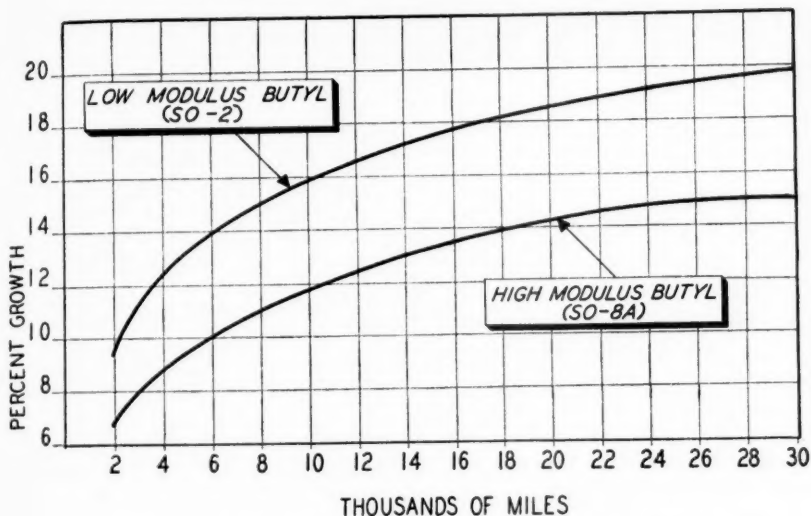


FIG. 1.—Comparison of growth of low-modulus Butyl and high-modulus Butyl tubes.

Figure 2 compares the progressive growth throughout 50,000 miles between a first-line black natural-rubber tube and a well compounded, well cured Butyl tube made from high modulus polymer (Table III).

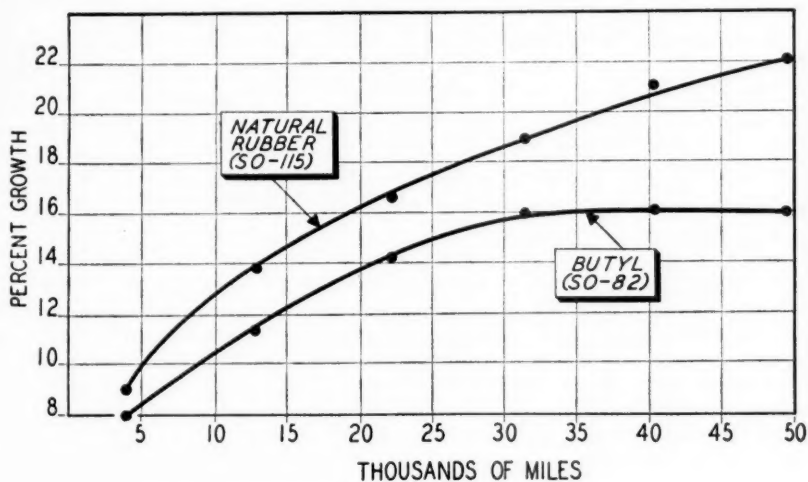


FIG. 2.—Comparison of growth of Butyl and natural-rubber tubes.

AIR HOLDING

The main function of an inner tube is to hold air. Before other polymers were available, natural rubber was considered to perform reasonably well as a gas barrier; it was used to make balloons, diaphragms, and gas masks as well as inner tubes. But inner-tube manufacturers have long recognized that there

TABLE III
COMPOUNDS USED IN PROGRESSIVE GROWTH TESTS

Butyl tube (SO-S2)		Natural-rubber tube (SO-115)	
Butyl	95	Smoked sheet	100
Polybutene ^a	5	Zinc oxide	3
Zinc oxide	5	FT black	55
Petrolatum	2	Stearic acid	2.25
Thiuram-type accelerator ^b	1	Process oil	3.8
Thiazole-type accelerator ^c	0.5	Paraffin	0.5
Sulfur	2	Sulfur	1.5
MT black	35	Accelerators	1.58
HMF black	15	Age-resister	1.15
Glycerol	1		
Polyac	0.1		

^a Polybutene in this compound was used as a processing aid.

^b See footnote a, Table I.

^c See footnote b, Table I.

is much room for improvement in the air-holding properties of natural-rubber inner tubes. Before the War, rubber companies conducted many experiments with materials which could be injected into natural-rubber inner tubes to improve their air-holding qualities. Automobile owners, as well as tube manufacturers, are aware of the fact that air diffuses through natural rubber; they are also aware that the rate of diffusion increases on aging.

Controlled road tests were carried on at the test fleet to determine the actual air-holding properties of Butyl tubes in service and to compare Butyl with natural-rubber tubes in this respect. In carrying out these air-holding tests, precautions were taken to ensure a minimum loss of air from the valve. A special measuring device was used to prevent loss of air during measurement. The tubes were kept in the tires for the life of the tires. These same tubes were then remounted in new tires and the test continued. One test was continued until five sets of tires had been worn out. When a new set of tires was applied, a 5-day (5000 mile) break-in period was allowed before regular air-holding measurements were recorded, so that errors caused by apparent loss of pressure due to tire growth would not be included in the data. At the end of the break-in period the tubes were reinflated to normal pressure. No air was added (except when tubes were remounted in a new set of tires) until one of the four tubes had fallen to 22 pounds pressure at room temperature. At this point all tubes were reinflated to the original pressure of 28 pounds at room temperature and the tests were continued. Thus no tire ever fell below 22 pounds pressure. It was realized that many car drivers permit the pressure in their tires to fall below 22 pounds, but for these test car conditions of overload and continuous high-speed driving it was considered dangerous to let the pressure get below that figure. The results that follow, then, are concerned with air losses only between an upper pressure of 28 pounds and a lower pressure of 22 pounds.

Figure 3 illustrates the air-holding superiority of Butyl inner tubes over natural-rubber tubes. Loss of air pressure in pounds per square inch is plotted against number of hours of air holding. This test was run on a Chrysler automobile operating at 60 miles per hour, 24 hours per day, 5½ days per week. Air-holding measurements were continued over week-ends while the car was standing in the garage. The test was run using 7.00 × 15 natural-rubber tires with two 7.00 × 15 black natural-rubber and two 7.00 × 15 black Butyl tubes.

Both the natural rubber and the Butyl tubes were of the best quality and were of recent manufacture. The test was considered complete when the set of tires had worn smooth. This occurred after 20,176 miles, which included 664 consecutive air-holding hours (approximately 28 days).

Other air-holding tests were run at the test fleet to observe the effect of various compounding changes in the Butyl inner-tube recipe. None of the changes studied so far had any influence on air-holding performance.

Air-holding tests run to date indicate that Butyl tubes hold air 8 to 10 times better than natural-rubber tubes. These ratios of 8 to 1 or 10 to 1 were established under severe test conditions. Informal tests, under conditions of driving and standing more nearly approaching normal practice, indicated a permeability ratio even more favorable to Butyl. These latter tests indicate that it will be necessary for the average motorist to reinflate his tires only two or three times a year.

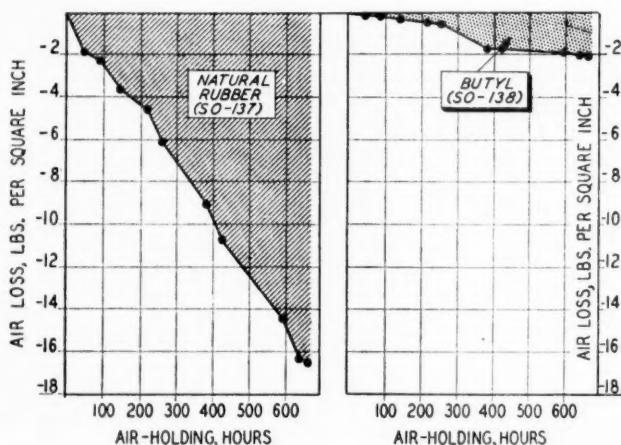


FIG. 3.—Comparison of air loss in Butyl and natural-rubber tubes after 20,176 miles of travel.

INFLUENCE OF BUTYL TUBES ON TIRE WEAR

Automobile manufacturers specify not only tire size but also optimum inflation pressure at which the tires should be maintained for safe and economical operation. Overinflation is undesirable. It reduces puncture and blow-out resistance, increases tire strain, causes rapid and uneven tread wear, and makes the car less comfortable to ride in. Underinflation also reduces puncture and blowout resistance. It increases tire strain and tire operating temperature because of increased flexing. Tread wear, driving safety, and ease of steering are also reduced by underinflation.

Since the superior air-holding properties of Butyl tubes make it a relatively simple matter to maintain proper inflation pressures, it was suggested that an overall increase in tread wear would result from the use of Butyl tubes. To test the validity of this proposition, tread wear was measured during the course of the air-holding tests.

Figure 4 illustrates the effect on tread wear when Butyl tubes are used in place of natural-rubber tubes. In this test two 6.00×16 black natural rubber and two 6.00×16 black Butyl tubes were mounted in four GR-S (S-3) 6.00

× 16 tires. The test was run on a Chrysler automobile traveling at 60 miles per hour, 24 hours per day, 5 days per week. All tires were reinflated to the original pressure of 28 pounds whenever any one of the tires fell below 22 pounds pressure at room temperature. The tires were rotated every 24 hours (approximately every 1000 miles) and tread wear measurements made every 48 hours (approximately every 2000 miles). This test occupied a period of 25 days from January 2, 1945, through January 27, 1945. It was necessary to reinflate the tires once during the test. This occurred at 9825 miles, at which point the tire containing the natural-rubber tube measured 20.5 pounds and the tire containing the Butyl tube measured 27.5 pounds at 65° F. The test was discontinued after 17,095 miles so that photographs could be obtained.

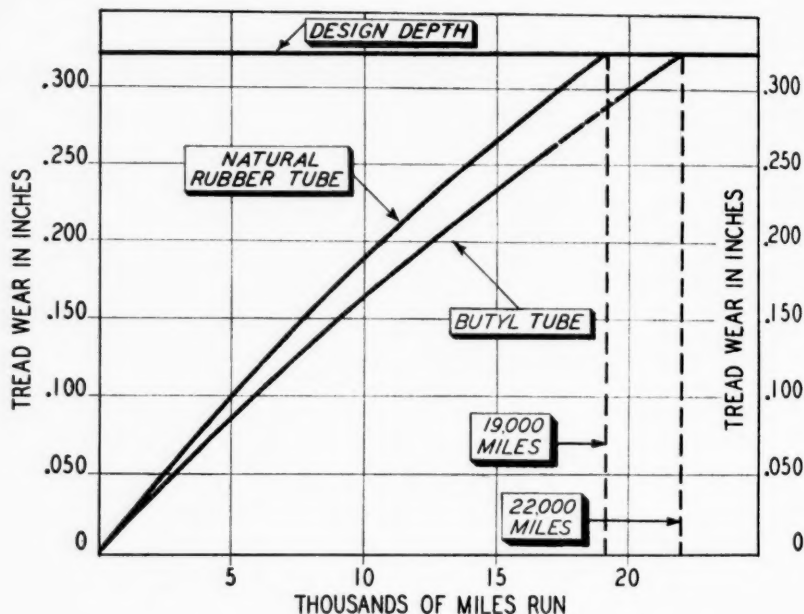


Fig. 4.—Comparison of tread wear of 6.00 × 16 GW-S(S-3) tires, with Butyl and natural-rubber tubes, at 60 miles per hour.

At this mileage the tires containing natural-rubber tubes were practically smooth. The actual condition of the tires at the completion of this test is shown by the photograph in Figure 5.

Figures 4, 6, and 7 are drawn by plotting the number of miles that the tires have been tested on the road against tread wear in inches. At any point on the curve the tread wear, commonly expressed as miles per mil, can be calculated. Since the tread wear is measured by gaging the depth of the nonskid grooves, the last portion of the curve must be extrapolated (shown by dotted lines). At this stage the depth of tread cannot be accurately measured because the tire is almost smooth.

In the test demonstrated by Figure 4, the tire containing a natural-rubber tube had a nonskid tread life of approximately 19,000 miles; the tire containing a Butyl tube, 22,000 miles.



FIG. 5.—GR-S tires with natural-rubber tubes (*left*) and Butyl rubber tubes (*right*) after 17,095 miles.

Figure 6 also illustrates the effect on tread wear when Butyl tubes are used in place of natural-rubber tubes. However, in this test four natural-rubber 7.00×15 tires were used in conjunction with two 7.00×15 black natural-rubber tubes and two 7.00×15 black Butyl tubes. The test procedure was exactly the same. This test was considered complete after 20,176 miles, at which point the tires containing natural-rubber tubes had worn smooth. This test occupied a period of 34 days from May 25, 1945, through June 27, 1945. It was necessary to reinflate the tires three times: once at 4835 miles and again at 6840 miles because of nail punctures, and finally at 14,180 miles; at that point the tire containing the natural-rubber tube measured 19.55 pounds and the tire containing the Butyl tube measured 25.2 pounds at 65°F .

One more control test was carried out to measure the relative tread wear when Butyl and natural-rubber tubes are compared. The conditions of this test were somewhat different from the previous two tests. Figure 7 shows tread wear when the test car was run at 40 miles per hour instead of at 60 miles per hour. Furthermore the tires were not reinflated until any one of them had fallen below 20 pounds pressure when measured at room temperature. The conditions of this test were adjusted so as to duplicate more closely driving conditions used by the ordinary motorist. Other conditions of the test, such as tire rotation, etc., were followed as in previous tests. Under these conditions the tire containing the natural-rubber tube had a nonskid tread life of

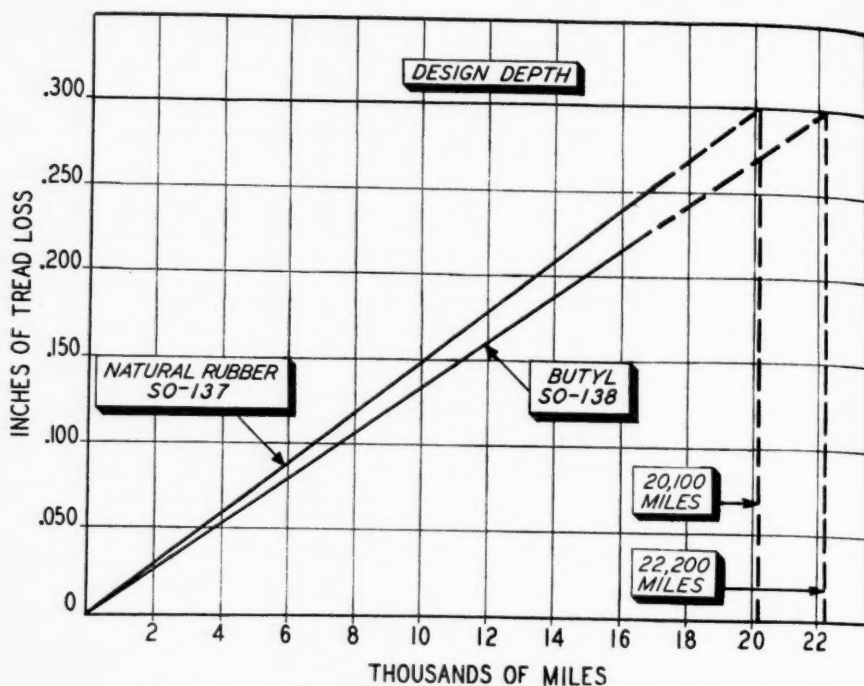


FIG. 6.—Comparison of tread wear of 7.00 X 15 natural-rubber tires with Butyl and natural-rubber tubes, at 60 miles per hour.

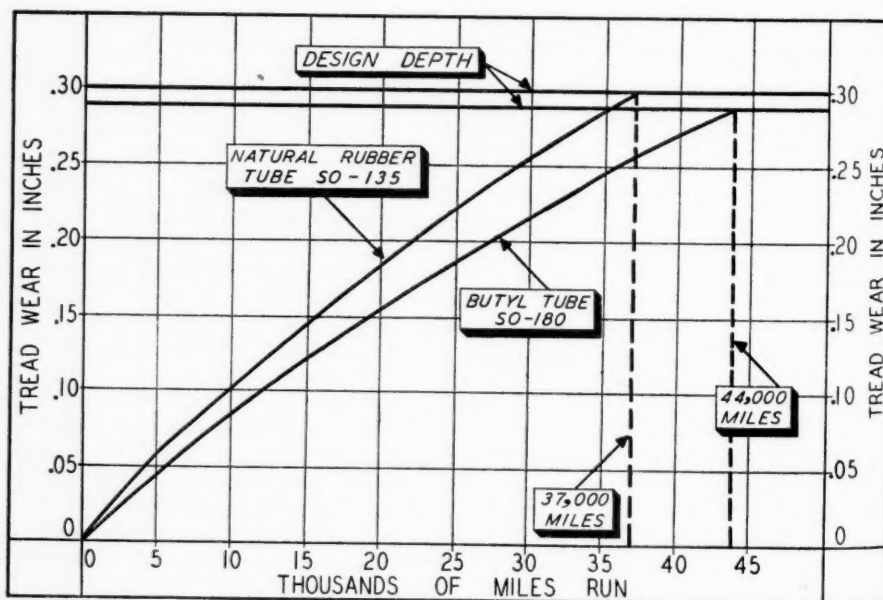


FIG. 7.—Comparison of tread wear of 7.00 X 15 natural-rubber tires with Butyl and natural-rubber tubes, at 40 miles per hour.

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approximately 36,000 miles, whereas the tire containing the Butyl tube had a nonskid tread life of approximately 43,000 miles. This difference—approximately 18 per cent—is greater than was the case when the test cars were traveling at 60 miles per hour. This is to be expected, since the tread life of a tire is much higher at slower speeds; therefore, under the conditions of this test, the tires containing the natural-rubber tubes were run for a longer increment of time at pressures lower than 28 pounds.

In interpreting these results one must bear in mind the speed at which the cars were traveling, the mileage run at underinflation and the minimum pressure allowed before reinflation, as these factors greatly influence the results obtained. It will be recognized that all these objective conditions depend on a subjective function—namely, the diligence of the car operator.

Aside from increased tread wear, there are indications that other advantages in tire performance are to be gained by the use of Butyl tubes. Rapid tire aging, caused by seepage of air from the tube through the tire, will result in ply separation, side-wall blisters, and reduced blowout resistance. This is particularly true when the tire casing makes an airtight seal against the wheel rim and so prevents air, which has permeated outward through the tube, from escaping by any route other than the body of the tire.

MAINTENANCE OF AGING PROPERTIES

The performance of an inner tube depends to a large extent on its ability to maintain original physical properties over long periods of time in service. The average automobile owner starts out with a new inner tube in a new tire. At this point the tube is well protected by the new tire and the possibilities of tire failures, such as punctures and blowouts, are at a minimum. However, as the mileage and age of tire and tube increase, tire failures become much more probable, and the protection afforded the tube by the tire decreases. Now the physical properties and characteristics of the inner tube increase in importance. If the inner tube is able to maintain its resistance to tearing, cutting, pinching, etc., it will afford a much greater margin of safety to the automobile driver.

Butyl inner tubes maintain their physical properties to a much higher degree than do natural-rubber tubes, not only under laboratory aging conditions but also after many miles of service.

Figure 8 compares the aging resistance (retention of properties) of a Butyl inner tube with a natural-rubber tube under two different types of laboratory aging conditions. Actual tube sections taken from a factory production run were used. The Butyl tube was of standard quality. The natural-rubber tube was of the best quality and was specifically compounded to withstand heat aging. (The tube compounds are the same as those of Table II.) The physical properties studied were modulus at 300 per cent elongation, tensile strength, ultimate elongation, and tear resistance. The retention of these physical properties after aging is compared. In the first aging test the Butyl and natural-rubber tube sections were suspended in a circulating air oven (Geer oven) for 7 days at 158° F. In the second aging test the tube sections were placed in an air bomb for 20 hours at 260° F. The superiority of the Butyl tube over the natural-rubber tube is evident.

In service aging, that portion of the tube under the shoulder and crown of the tire is subject to the greatest heat and the greatest flexing. A deterioration in physical properties must therefore be sought in the shoulder and crown area. Just as a chain is no stronger than its weakest link, so an inner tube is no more serviceable than its weakest part. It makes little difference if an inner

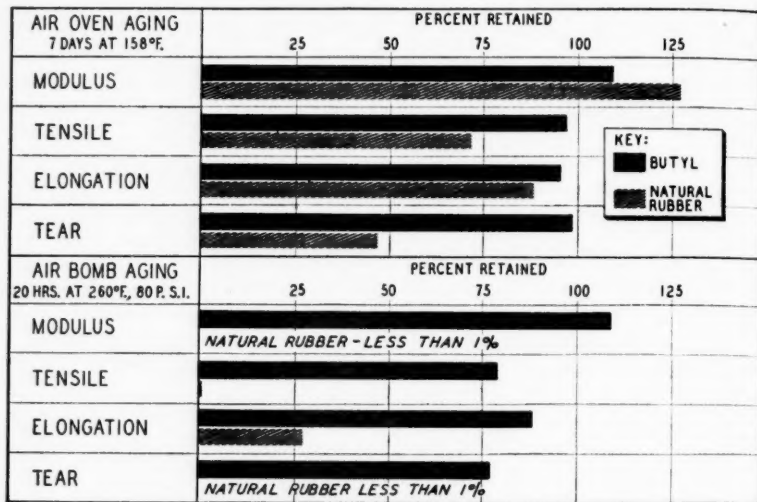


FIG. 8.—Laboratory aging of Butyl and natural-rubber tubes.

tube has maintained all its tensile strength and tear resistance at the base or rim side if it has lost most of its tensile strength and tear resistance under the shoulders of the tire. Under these conditions, for practical purposes, it is as if all portions of the inner tube had deteriorated to a like degree.

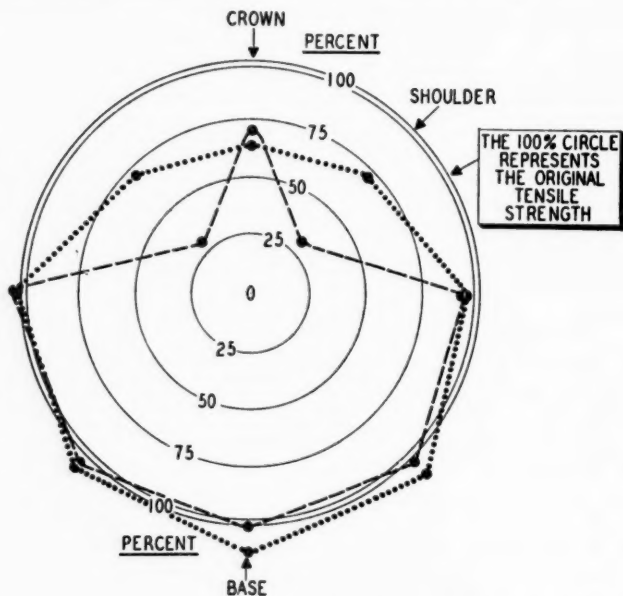


FIG. 9.—Tensile retention of road-tested inner tubes in 6.00 × 16 GR-S tires after 50,000 miles at 40 miles per hour.
 --- Natural-rubber tube (SO-116)
 Butyl tube (SO-82)

Figure 9 shows the deterioration in tensile strength of a Butyl tube compared with a natural-rubber tube after 50,000 miles of road testing at 40 miles per hour. The compounds used in each of these tubes are again the same as those of Table II, and the same as those used in the laboratory aging study.

To plot this curve, dumbbell specimens were cut from a new, unused tube at various cross-sectional positions—for example, crown, shoulders, base, etc. The tensile strength values of these dumbbells were determined. These values were plotted on polar coordinate paper at locations corresponding to their positions on the tube itself. With new tubes, either Butyl or natural rubber, the result is a circle, since a new tube is equally strong at all points. Companion tubes made from the same batch of rubber, given the same cure, etc., were placed on cars for road service. At the end of 50,000 miles dumbbell specimens were cut from shoulders, crown, base, etc., as had been done on the new tubes. The values determined on these specimens were plotted on the same polar coordinate paper. They are shown by the broken lines. Figure 9 gives a visual comparison in terms of tensile strength throughout the cross-sectional area, between Butyl and natural-rubber tubes after service testing.

Even with this heavy-duty natural-rubber tube the deterioration of tensile strength under the shoulders of the tire is marked; although the Butyl tube also deteriorated in tensile strength through the crown and shoulder area, it deteriorated to a much lower degree than did a natural-rubber tube.

PUNCTURE AND BLOWOUT RESISTANCE

When a nail or other similar object penetrates a tire and punctures the inner tube, the ability of the tube to resist tearing at the point of rupture is of great importance as an economical consideration and from the viewpoints of safety and convenience. Tearing at the point of rupture results in rapid deflation, similar in results to a blowout of the casing. Tearing to even a slight degree results in deflation sufficiently rapid to prevent the driver from reaching a service station, where he can obtain assistance in changing the tire. The final size of the rupture determines whether the tube is repairable or if it must be discarded in favor of a new tube.

Initial tests to study the puncture and blow-out (tear) resistance of Butyl tubes involved the use of a special air pressure measuring device. This device can be attached to a tire and measures continuously the air pressure as the tire travels over the road. By means of this measuring device it was possible to compare loss of air after puncturing Butyl and natural-rubber tubes.

The procedure in these tests is as follows: A Chrysler automobile equipped with the continuous air pressure measuring device is used; the tubes to be tested are mounted in tires which have been worn smooth in previous tests; nails are driven into the tires; and the car is driven at a speed of 60 miles per hour until the air pressure in any tire measures 10 pounds. Air pressure readings are recorded at 2-minute intervals. At the completion of the test the tubes are dismounted and the condition of the ruptures are examined.

Using new natural-rubber and new Butyl tubes, tests were run using (1) a tenpenny nail driven in at the crown and removed, (2) a tenpenny nail driven in the shoulder and removed, (3) a tenpenny nail driven in half way at the crown and allowed to remain, and (4) a large staple (same gage as tenpenny nail) driven into crown and allowed to remain. From these tests it was concluded that new Butyl tubes offer the same puncture and blow-out (tear) resistance as new natural-rubber tubes.

The next series of tests compared Butyl and natural-rubber tubes that had already been in service. Butyl tubes which had been run 35,000 miles under normal conditions before being tested behaved fully as well as new Butyl tubes. No reduction in puncture or tear resistance could be noted. All ruptures in the Butyl tubes, either new or used, were small enough to be repairable. All of the used Butyl tubes were run at least 15 miles before the minimum pressure of 10 pounds was reached, and many of them could have been driven over 100 miles. There was no indication that any puncture would have caused a blow-out type of tear.

Tests on used natural-rubber tubes were made by using rubber tubes that had completed 25,000 miles of normal service. The same method of testing was employed as had been used on the Butyl tubes; that is, nails were driven into the tires while the car was stationary, and then the car was set in motion and accelerated to 60 miles per hour. In this case all tires containing used natural-rubber tubes went flat in less than 5 miles. Examination revealed tears in the tube at the punctured area. The dimensions of some of these tears were such that it would have been impossible to repair them. The conclusion was reached that if the test car had been traveling at a high rate of speed when the puncture occurred, the tire would have gone flat almost instantaneously.

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- ⁴ In the terminology of the Rubber Reserve Co., fast-curing Butyl is Y-15 or Y-25; this type is more highly unsaturated.

LIGNIN FOR REINFORCING RUBBER *

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The lignin used in this work comes from pine wood, in which it occurs as one of the incrusting substances associated with cellulose fibers. The chemical structure of lignin as found in nature is not yet established, and it is probable that the product is further modified by the recovery processes used. Abundant evidence has accumulated, however, in the course of manufacturing hundreds of tons of the material that the product is reproducible and uniform in grade. The lignin so made reacts as if it always had the same fundamental chemical structure with minor substituents. The prevailing opinion today is that this structure is cyclic and consists of various polymers of a unit of $C_{41}H_{32}O_6$, containing in addition about eight to ten hydroxyl or methoxyl groups. The lignin used averaged about four hydroxyl and four methoxyl groups for $C_{41}H_{32}O_6$ comprising a unit molecular weight of about 840. This particular lignin contained about 1 to 2 per cent of sulfur, which appeared to exist principally in a stable thio form. One of the hydroxyl groups appears to be phenolic, for it reacts with alkalis and many organic compounds.

The lignin used for reinforcing rubber was made from the black liquor available at a large southern sulfate pulp mill. In the process used, the black liquor, which contains the lignin dissolved as a sodium compound, is acidified. The lignin precipitates and is filtered and washed free of occluded impurities. On drying, a brown free-flowing powder is obtained which is easily handled in bags, barrels, drums, or hopper cars. The specific gravity of lignin is 1.3, and it has a packed density of 25-30 pounds per cubic foot.

This lignin from the sulfate process is representative of more than a million tons potentially available annually from sulfate and soda pulp mills in the United States.

LIGNIN AND RUBBER

Lignin as a reinforcing agent for synthetic rubber is a development of wartime research to augment the supplies of carbon black and other fillers for rubber. Although the completion of the research came too late to be of commercial value during the war, it is being carried over into peacetime work, where it will enhance the properties of rubber products using other pigments. It shows promise of strengthening the position of synthetic rubber with respect to natural rubber, and thus making the industry more independent of foreign natural rubber supplies.

The obstacles preventing the prompt war application of lignin for reinforcing rubber have now been largely overcome. The process for the manufacture of lignin itself was the subject of considerable development work before commercial production could be attained. The rigidity of the government program

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in supplying the large quantities of synthetic rubber for essential military purposes precluded the investigation of the minor changes required in the large rubber manufacturing plants. Compounding and curing of the lignin GR-S coprecipitates also required some study because of slightly varying characteristics. With the progress that has been made in all directions, the use of lignin for reinforcing synthetic rubber is now assured.

Lignin is a reinforcing pigment for rubber which is particularly adapted to the newly developed processes of coprecipitation of the pigment with synthetic or natural rubber. Because of the high degree of dispersion of the lignin in the rubber, little milling time is needed for completing the breakdown of the rubber. Generally it has been observed that, where crude rubber required 20 minutes for breakdown, the lignin latex coprecipitate could be milled in 2 to 4 minutes. The time required for adding the filler is also eliminated.

Among rubber-reinforcing agents, lignin is unique in that it is soluble in aqueous alkali, such solutions being compatible with the latex emulsions in all proportions. Dispersing agents commonly used with insoluble pigments are thus eliminated. Furthermore, it is possible to precipitate both the lignin and the rubber from the mixture with acids in the same pH range, as is commonly used in coagulating or precipitating latex alone.

Alkaline aqueous lignin solutions are likewise good dispersing mediums for carbon black and other pigments, and the resulting dispersions are compatible with rubber latices. Thus the dispersed insoluble pigment may be mixed with latex, and the mixture then coprecipitated with acid or other precipitating agent; the result is a well dispersed coprecipitate of carbon black or other pigment, lignin, and rubber.

COPRECIPITATION OF LIGNIN AND GR-S

The process by which lignin and lignin-dispersed pigments are coprecipitated with rubber is similar to that commonly used for synthetics of the GR-S type. Following is a stepwise outline of the procedure for preparing a coprecipitate containing 50 pounds of lignin and pigment per 100 pounds of GR-S. The quantities of materials required for other loadings are given in Table I.

TABLE I

MATERIALS REQUIRED FOR VARIOUS LOADINGS OF LIGNIN
(Basis, 100 pounds of GR-S, or 400 pounds of GR-S latex)

Lignin loading (lbs.)	5	10	25	50	100	150	200
Water for soln. (lbs.)	13.5	27	68	135	270	405	540
50% caustic soda (lbs.)	1.0	2.0	5.0	10.0	20.0	30.0	40.0
60% Bé. sulfuric acid (lbs.)	4.2	5.4	13.2	23.4	43.8	64.2	84.6

1. *Lignin solution:* (a) Suspend 50 pounds of lignin and pigment in the desired proportion of 135 pounds of water; (b) add 50 per cent caustic soda solution corresponding to the lignin loadings. This solution then contains 25 per cent lignin and pigment by weight.

2. *Latex:* 400 pounds GR-S latex, type 1, 25 per cent rubber solids.

3. *Acid solution:* (a) Add 60° Baumé sulfuric acid corresponding to the lignin loading to 330 gallons of water; (b) heat to 150° F.

4. *Coprecipitation:* (a) Add the lignin-pigment mixture to the latex with stirring; (b) add the lignin-pigment-latex mixture to the acid solution with stirring; (c) filter; (d) wash the coprecipitate with water until the pH of the wash water is at least 5.

5. Dry the coprecipitate in air at 160–170° F.

For easy comparison of normal latex coagulation, coprecipitation with lignin and coprecipitation with lignin-dispersed pigments, flow sheets for each process are shown in Figures 1, 2, and 3.

Curing coprecipitates.—Since lignin is slightly acidic in nature, its presence retards somewhat the cure where the usual alkaline accelerator chemicals such as diphenylguanidine or benzothiazoyl disulfide are used. This may be readily overcome by increasing the amount of a base present—for example, by increasing the quantity of zinc oxide in the compounding formula or by using

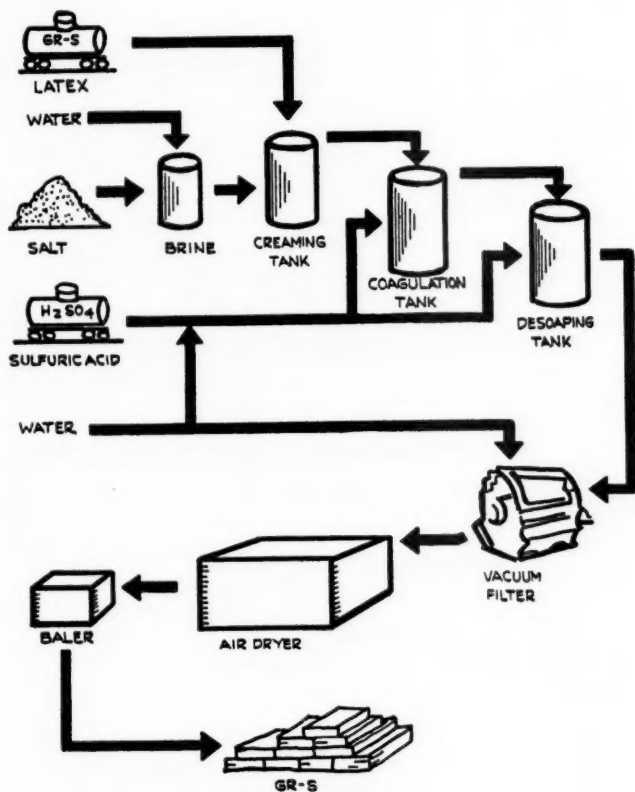


FIG. 1.—Flow sheet of normal GR-S latex coagulation

more or stronger accelerator chemicals. Copper diethyldithiocarbamate has been found to be very effective in combination with benzothiazoyl disulfide for this latter method (Table II). Another effective combination is mercapto-benzothiazole as primary accelerator, with tetramethylthiuram monosulfide as activator. No doubt other accelerators can also be found.

Another method of lowering the curing time is to add alkaline substances such as amines or compounds of Groups I, II, or III metals which form salts with the acidic lignin, preferably to the wet coprecipitate. Raising the pH of the coprecipitate in this way from 6 to 7.1 by reaction with lime water lowers

TABLE II
EFFECT OF VARYING AMOUNTS OF ACCELERATOR ON CURE OF COMPOUNDS

Formula, parts		Copper diethyl-dithio-carbamate (part)	Optimum cure at 292° F (min.)	Optimum tensile strength (lb. per sq. in.)
Coprecipitate (50 lignin + 100 parts GR-S)	150	0.1	80	2500
Pine resin	5	0.2	60-70	2500
Zinc oxide	5	0.3	20-60	2650
Benzothiazoyl disulfide	1.5	0.4	30-40	2700
Sulfur	2	0.5	20	2650

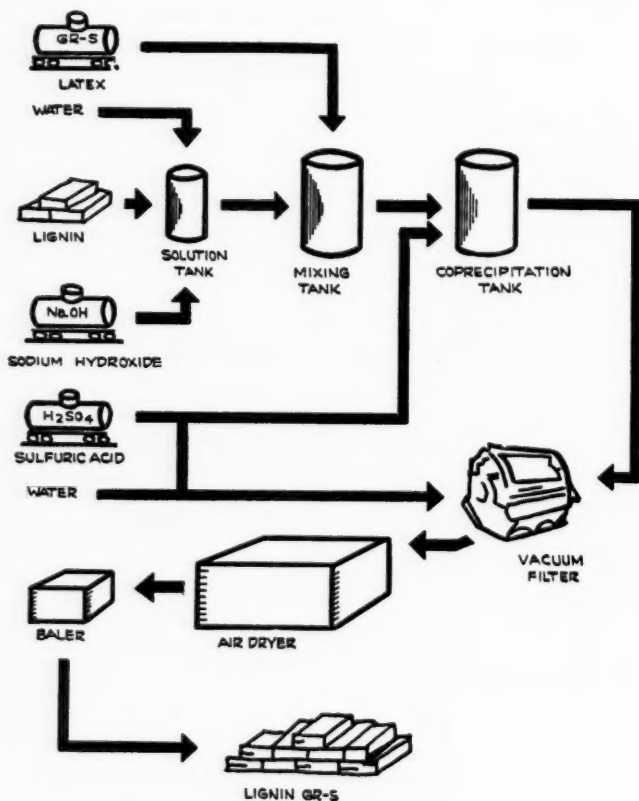


FIG. 2.—Flow sheet of coprecipitation with lignin

the optimum curing time from 80 to 50 minutes. A further increase of pH to 7.3 lowers the curing time to 30 minutes.

Properties of cured coprecipitates.—The tensile strengths of rubbers reinforced with coprecipitated lignin are comparable with those obtained using carbon black as filler. Figure 4 shows typical stress-strain and other properties

of variously loaded lignin compounds prepared according to the formulas of Table III.

TABLE III
FORMULAS OF LIGNIN-REINFORCED GR-S COMPOUNDS
(IN PARTS BY WEIGHT)

GR-S	100	100	100	100	100	100	100	100
Lignin	10	25	35	50	70	100	125	150
Pine resin	5	5	5	5	5	5	5	5
Zinc oxide	5	5	5	5	5	5	5	5
Benzothiazoyl disulfide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Copper diethyldithiocarbamate	0.06	0.15	0.21	0.3	0.42	0.6	0.75	0.9
Sulfur	2	2		2	2	2	2	2

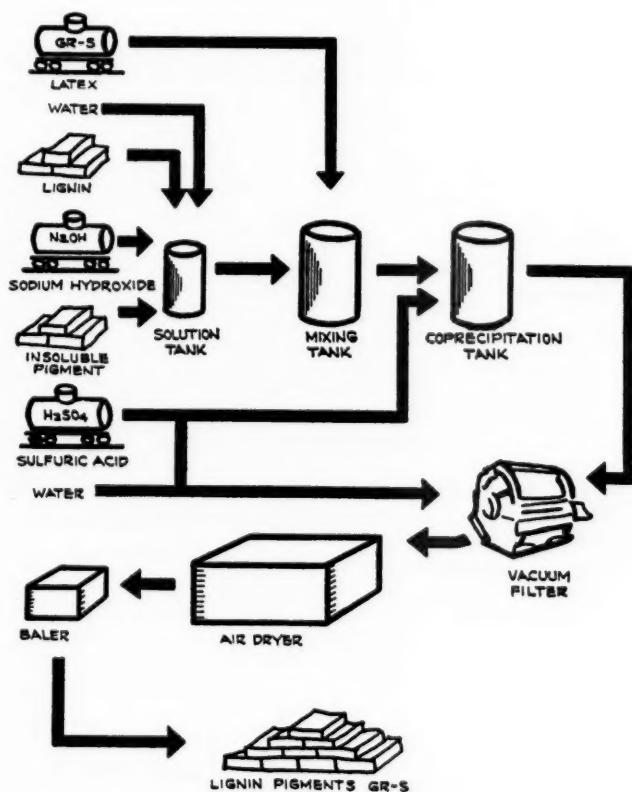


FIG. 3.—Flow sheet of coprecipitation with lignin-dispersed pigment

COMPARISON OF LIGNIN AND OTHER PIGMENTS

Figures 5 and 6 compare the physical properties obtained with lignin and various other pigments in GR-S. Table IV gives the formulas for this test. The volume loadings of 38.5 and 77 volumes of the pigments are equal to 50 and 100 parts, respectively, of lignin by weight.

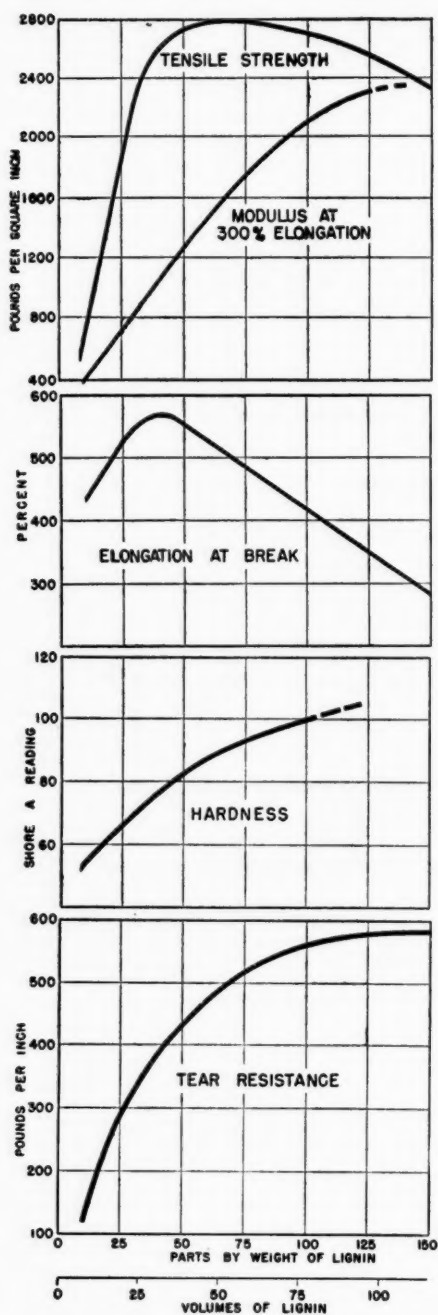


FIG. 4.—Tensile strength, 300 per cent modulus, elongation at break, Shore A hardness, and crescent tear resistance of lignin-reinforced GR-S compounds

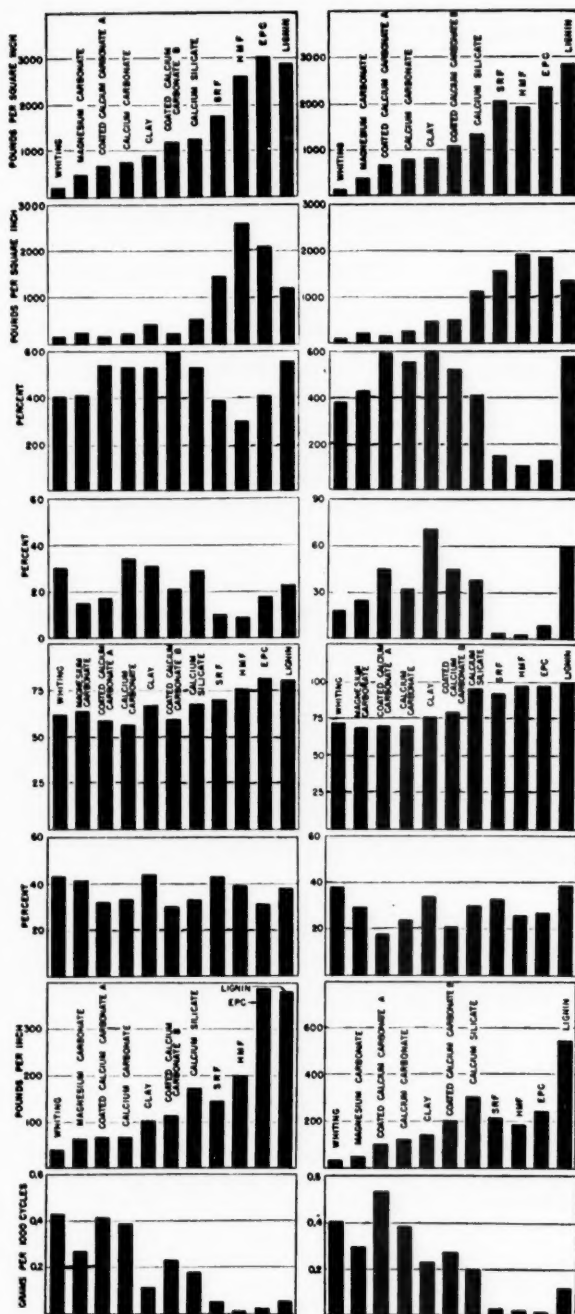


Fig. 5.—Properties of GR-S with 38.5-volume loading of lignin

Fig. 6.—Properties of GR-S at 77-volume loading of lignin

TABLE IV
FORMULAS (IN PARTS BY WEIGHT) OF COMPOUNDS REINFORCED WITH
LIGNIN AND OTHER PIGMENTS

GR-S	100	100	100	100
Lignin	38.5 ^a	77 ^a
Pigment	38.5 ^a	77 ^a
Zinc oxide	5	5	5	5
Benzothiazoyl disulfide	1.5	1.5	1.5	1.5
Copper diethyldithiocarbamate	0.3	0.6	0.1	0.1
Stearic acid	1.0	1.0	1.0	1.0
Coal tar	8	8	8	8
Sulfur	2.5	2.5	2.5	2.5

^a Volume loading.

These diagrams illustrate the fact that lignin as a reinforcing agent for GR-S develops novel properties in the vulcanizate. At the loading of 38.5 volumes, tensile strength, hardness, and tear resistance are of the same high order of magnitude as easy-processing channel black compounds; the 300 per cent modulus is somewhat lower and the elongation correspondingly higher. Although set at break, Bashore resilience, and abrasion loss are not so good as for the carbon-reinforced vulcanizates, they are superior in most cases to compounds containing inorganic pigments.

At 77-volume loadings, the properties of the lignin-reinforced vulcanizates are outstanding. The tensile strength of the lignin GR-S is 500 pounds per square inch higher than that of EPC, the next best pigment, and does not differ appreciably from the 38.5 volume loading. Elongation is also about the same as at the lower loading; the modulus is somewhat lower and considerably lower than that of the carbon blacks, all of which broke at elongations between 100 and 200 per cent. The tear resistance of 550 pounds per inch at the high loading is 250 pounds higher than that with any other pigment.

MODIFICATION OF STANDARD COPRECIIPITATION

When ammonium hydroxide or a volatile amine such as morpholine is used for solution of the lignin, a combination of aluminum sulfate, acetic acid, and heat may be substituted for sulfuric acid for coprecipitation. The alum and acetic acid coagulate the rubber, and the heat decomposes the lignin-amine compound. Coprecipitation may also be induced by either freezing or evaporation.

Before the wet coprecipitate of lignin and rubber is dried, it may be further homogenized by milling in any of the commonly used rubber mills. This results in an even finer particle size because the lignin, as precipitated and before drying, occurs as aqueous gel particles which are readily subdivided by any shearing action. The wet crumb may then be dried and milled in the usual manner.

This property of lignin of being soluble in and gelling in alkaline solutions permits its dispersion with rubber latex. The lignin may be added to the latex as an aqueous slurry, and a thorough mixture may be obtained by agitation. When, as is usual, the pH of the latex is on the alkaline side, the lignin reacts and at least partially dissolves; the pH is thereby lowered to a point where the rubber precipitates and, in effect, causes coprecipitation. Any of the lignin not dissolved is readily dispersible and subdivisible in subsequent wet milling operations. Even dry lignin in limited quantities, when mixed with latex, will similarly become either dissolved or gelled,

LIGNIN DRY-MILLED WITH RUBBER

Because of its property of undergoing subdivision in the gelled state by shearing action, lignin in the gelled state may be added to either crude natural or synthetic rubber by milling. Lignin in the gelled state is available (1) from the lignin before drying, (2) by soaking dried lignin in water, (3) by soaking or grinding with sufficient alkaline solution or other solvent (*i.e.*, dioxane, ethyleneglycol, etc.), or (4) the lignin may be mixed with a sufficient quantity of a fugitive alkali such as ammonia or morpholine, with a polymerizable chemical such as aniline or aniline-furfural mixture, or with chemicals which, during curing, react with either the lignin or the rubber, such as toluidine or cresol.

SUMMARY OF ADVANTAGES

Lignin should therefore be considered as a pigment for developing specific properties in rubber and not as a substitute for other pigments. Its use in conjunction with other pigments to obtain desired combinations of properties is also suggested. In brief, the characteristics of lignin as a reinforcing agent for rubber are as follows:

Tensile strength comparable with those obtained using carbon blacks at low loadings, and higher tensile strength and tear resistances at high loadings.

Lower specific gravity than other common reinforcing agents since it is 70 per cent as heavy as carbon black, 50 per cent as heavy as clay or calcium carbonate, 33 per cent as heavy as titanium dioxide, and 23 per cent as heavy as zinc oxide.

Wide color possibilities, retaining high tensile strength.

Lowering of processing time by reducing the breakdown time and eliminating addition of the filler or reinforcing agent.

ACKNOWLEDGMENT

The authors wish to express their appreciation of the technical assistance of Walter K. Dougherty in conducting many of the tests and of the staff of Foster D. Snell, Inc., in confirming some of the results. The authors are greatly indebted to the many members of the Development Department of the West Virginia Pulp and Paper Company, who coöperated in supplying the lignin and in preparing for the first time batches of as much as 1000 pounds of lignin-GR-S coprecipitates. Also gratefully acknowledged are the encouragement, advice, and assistance rendered by the personnel of various government agencies, especially E. R. Gilliland and C. W. Perry, then of the Office of Rubber Director, and R. W. KixMiller and A. E. Boss, then of the Rubber Reserve Company.

SUMMARY

Lignin, as made from the waste black liquor of the sulfate wood pulp process, is an effective reinforcing agent for synthetic or natural rubbers when incorporated into latex by the coprecipitation or master-batching procedure. GR-S, reinforced in this manner with 38.5 volumes of lignin, yields vulcanizates having a tensile strength of 2900 pounds per square inch and a tear resistance of 380 pounds per inch, values exceeded only with channel black. With 77 volumes loading the tensile strength of 2800 pounds per square inch and tear resistance of 550 pounds per inch are higher than those for any other pigment

tested. In abrasion resistance lignin vulcanizates are between carbon blacks and the common inorganic fillers. Shore hardness values are close to those for channel black. Lignin-reinforced rubbers weigh appreciably less per unit volume, owing to the low specific gravity, 1.3, of lignin. The brown color of lignin permits a wide color range, without sacrifice of mechanical properties, by blending with white pigments. Lignin coprecipitates require only a brief milling time for complete mastication. Details are given on the preferred procedure for preparing master batches of lignin and GR-S. Other suggested incorporation procedures made possible by the colloidal properties of lignin are reviewed.

DISPERSOIDAL ANALYSES OF HEVEA LATEX *

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In the latex of *Hevea brasiliensis* the rubber particles occur as a polydisperse phase, their diameters varying from about 0.1 to 3 microns. In an investigation carried out by the author¹ on the influence of the size of particle of *Hevea* latex on the composition and properties of rubber, it was found necessary to have at one's command an accurate but not too laborious method of dispersoid analysis.

In the case of a polydisperse colloid such as latex, it is relatively useless to express the degree of dispersion as the average particle diameter, or as the number of particles per unit weight of latex; it can only be characterized accurately by a distribution curve which reproduces the number, surface, volume or weight of the particles as a function of the particle diameter².

Two methods have been used: (1) photomicrographic analysis, and (2) sedimentation analysis.

1. *Photomicrographic analysis*.—This analysis was originally worked out by Green³ for the determination of the particle size in fillers. Lucas⁴ and McGavack⁵ performed a dispersoid analysis of *Hevea* latex according to this method. Green employed the ultraviolet microscope, with which particles with a diameter to 0.1μ could be measured.

In the measurements carried out by the present author, use was made of an apochromatic objective, NA. 1.40, 60 \times , combined with a compensating ocular 10 \times , with a total magnification on the ground glass of the camera of 685 \times . This magnification was sufficient for the purpose, since sharpness of image and resolving power were such that the contours of the particles were sharply projected, even of those with dimensions near the border of the resolving power. Various precautions had indeed to be taken⁶, such as accurate centering and adjustment of illumination and optical system, complete absence of vibration, the use of a blue filter, and very contrasting and fine-grained plates, mainly sensitive to blue and violet light (Gevaert plates for graphic processes extra, 25 H and D).

Preparations were made from the latex sample to be investigated after it had first been diluted with water until its rubber content was 5 per cent, and then with a warm 5 per cent gelatin solution to about 0.5 per cent, to prevent currents in the liquid and to retard the Brownian motion. Figures 1 to 4 show several photographs of a preserved latex sample A and several fractions of different average particle size obtained from it. The negatives were projected in an enlarging apparatus on millimeter paper to a total magnification of 5400 \times , the smallest particles visible on the negative having a diameter of at least 1 mm. in the projection. With a sharply pointed pencil the diameter of

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the particles was now plotted on the paper, in a horizontal direction in all cases. The lengths of these lines were read off later and arranged in columns.

Three preparations were made of the latex sample in question, and two photographs of each preparation, numbered A1 to A6. Table I gives a survey of the results of the measurement for latex A (cf. Figure 1). The values of the diameter in mm. were recalculated in the second column to the values in μ , taking into account a total magnification of $5400\times$. In column 10, for increasing values of D , the total number of particles N in the six photographs

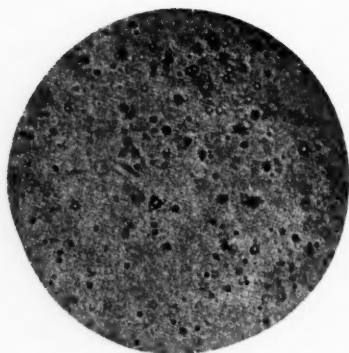


FIG. 1.—Latex A.

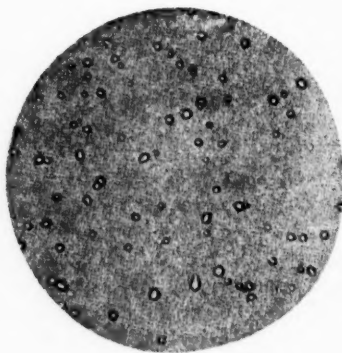


FIG. 2.—Fraction 1.



FIG. 3.—Fraction 3.

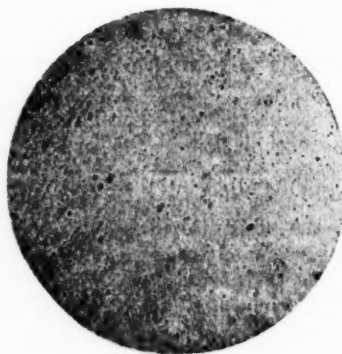


FIG. 4.—Fraction 7.

is given. From N , in the manner indicated, the distribution function $N(D)$ was calculated, expressed in percentage of the total number of particles. From the value of N and D the volume of the particles in every class was calculated (assuming them to be spherical), and from this value the distribution function $V(D)$ was calculated, expressed in percentage of the total volume of the particles. From these data Figure 5 was drawn, which gives the number, surface (calculated in a similar way), and volume-distribution curves of the particles in this latex according to their diameter.

TABLE I
DIMENSIONS OF PARTICLES IN LATEX A

Diameter in mm.	Diameter in μ	Average value of diameter	Number of particles per photograph						N	N \times D	N in %	N(D) in %	Vol. $\frac{\pi D^3 N}{6}$	V in %	V(D) in %	
			A ₁	A ₂	A ₃	A ₄	A ₅	A ₆								
1-2	0.19-0.37	0.28	9	22	35	4	32	48	150	42	8.9	8.9	1.7	0.3	0.3	
2-3	0.37-0.56	0.46	36	92	93	49	99	110	479	221	28.6	37.5	24.4	5.0	5.3	
3-4	0.56-0.74	0.65	49	67	99	47	55	53	370	241	22.0	59.5	53.4	10.8	16.1	
4-5	0.74-0.92	0.83	40	57	69	30	50	48	294	244	17.5	77.0	83.2	16.9	33.0	
5-6	0.92-1.11	1.02	43	44	45	24	38	26	220	224	13.2	90.2	122.1	24.8	57.8	
6-7	1.11-1.30	1.20	17	13	24	13	16	10	93	112	5.5	95.7	84.8	17.2	75.0	
7-8	1.30-1.48	1.39	11	11	11	2	11	3	49	68	2.9	98.6	68.8	14.0	89.0	
8-9	1.48-1.66	1.57	4	5	4	2	2	2	19	30	1.1	99.7	38.8	7.9	96.9	
9-10	1.66-1.85	1.76	1	—	1	—	2	—	4	7	0.2	99.9	11.5	2.3	99.2	
10-11	1.85-2.03	1.94	—	—	—	—	1	—	1	2	0.1	100.0	3.9	0.8	100.0	
Average values			210	311	381	171	306	300	1679	1191	100.0	492.6	100.0	$V_m = 0.29\mu^3$		
									$D_m = 0.71\mu$							

For various reasons, however, the photomicrographic dispersoidal analysis proved to be a method which cannot be recommended for the investigation of latex.

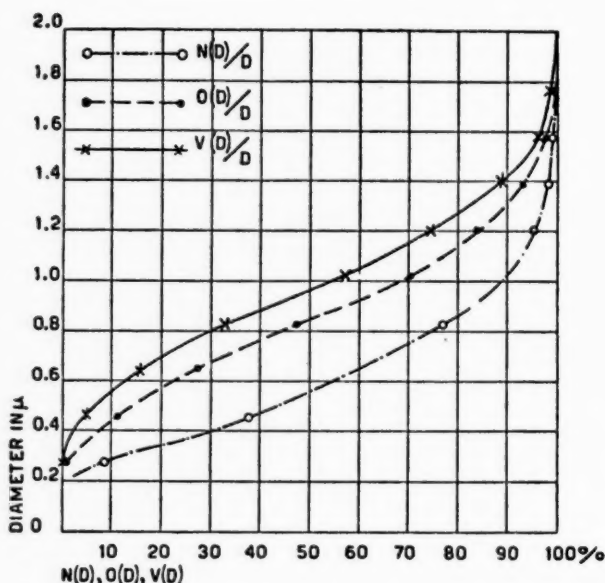


Fig. 5.—Distribution curve of latex A.

1. Due to the limited resolving power of the microscope, particles smaller than about 0.3μ were not measured at all, and those from 0.3 to 0.4μ only in part. In the investigation in question, however, the exact determination of the volume percentage of these smaller particles was of great importance.

2. Even with proper sharpness of image of the photomicrographs, the contours lost their sharpness on enlargement of the negative and, as a result, the measurements involve a relatively large error. In addition, in photographing such preparations all the particles are not situated in the same plane. On sharp focussing on a given layer, the particles which are situated slightly below or above this layer give a less sharp image, and their diameter is not measured accurately, and often too large.

3. The volume-distribution curve, which is the most characteristic, must here be calculated from the number. Such a determination is inaccurate unless a very large number of measurements is performed.

4. The method is very laborious and is not suited to a series of investigations.

2. *Sedimentation analysis.*—By this term is meant the determination of the particle size of a suspension by a study of the sedimentation of the particles with the application of Stokes' law. Stokes' law gives the velocity dx/dt with which a spherical particle of radius r and specific gravity d moves under the influence of gravity g in a liquid of specific gravity d_{v1} and viscosity η :

$$\frac{dx}{dt} = \frac{2}{9} r^2 g \frac{d - d_{v1}}{\eta} \quad (1)$$

For a valid application of this law⁷, the moving particles must be spherical. The deviation from the spherical form, which is only slight for most of the rubber particles in *Hevea* latex, was also disregarded in the photomicrographic analysis. On applying this law to a dilute suspension, not too dilute for the particles to affect each other's motion, it is more accurate to use the specific gravity and viscosity of the suspension instead of those of the medium.

a. Choice of the conditions.

Before passing on to the choice of a suitable method, it is first necessary to have some idea of the velocity with which the rubber particles in latex are displaced under the influence of gravity. Since the specific gravity of the particles is smaller than that of the surrounding serum, they rise under the influence of gravity, and one speaks in this case of creaming instead of sedimentation. In Table II the height of rise of rubber particles of different

TABLE II
HEIGHT OF RISE IN CM. OF RUBBER GLOBULES AFTER A
CREAMING TIME OF 10 DAYS

Diameter D in μ	Height of rise in cm. at a value of A of		
	0.3	0.15	0.075
0.2	0.06	0.12	0.24
0.5	0.4	0.8	1.6
1.0	1.6	3.1	6.2
2.0	6.2	12.5	25.0
3.0	14.0	28.0	56.0

diameter is calculated with the help of Stokes' law after a creaming time of 10×24 hours. The viscosity of the medium is taken as 1.5×10^{-2} poises⁸. The factor $\eta/d_{v1} - d = A$ for latex with about 10 per cent of rubber at 20°C amounts to about $\frac{1.5 \times 10^{-2}}{0.997 - 0.912} = 0.18$, but, as will appear, it may be altered by altering the circumstances. It is for that reason that in the table the heights of rise are calculated for different values of the factor A .

From these figures it appears that, at a value of A of 0.15, appreciable creaming first takes place with a diameter of 1μ , but that on decrease in A the velocity of creaming increases. If the requirement is made that in carrying out the dispersoidal analysis the creaming time shall not amount to more than 10 to 14 days, the height of rise of particles with a diameter of about 0.5μ is about 2 cm. with a value of A of 0.075.

After this orientation the usefulness of the different methods of sedimentation analysis as applied to rubber latex may be considered.

In the investigation of a column of liquid of a polydisperse colloid in which differences of concentration have resulted from sedimentation, three methods of investigation can be distinguished, according to Berg⁹.

1. The amount of substance which settles out of a liquid column in the time t on an area O lying h cm. below the surface of the liquid can be determined. The sediment consists of all the particles with a diameter greater than D which have been displaced over h cm. in the time t . Smaller particles also occur in amounts which depend on their diameters.

Odén's balance works on this principle. Aside from the complexity of the apparatus, the method cannot be employed for latex, which creams instead of settling.

2. After a time t , the amount of substance can be determined in a column of liquid, the area of whose base is O , h cm. below the surface of the liquid. In this column particles with a diameter greater than D no longer occur. Such particles have been displaced over a distance greater than h in the time t ; particles with a diameter smaller than D have partially disappeared, in amounts which depend on their diameters.

In the methods described under 1 and 2, the weight-distribution curve has to be derived from the experimentally determined values by means of fairly complicated calculations; graphic solution may, however, simplify the calculation very much¹⁰.

This principle is employed in the apparatus of Wiegner, Ostwald, von Hahn, et al. The change is measured in the hydrostatic pressure of a liquid column of the suspension as a result of sedimentation. Stamm¹¹ also applied this principle to the determination of particle size in emulsions in which the disperse phase was lighter than the liquid medium.

For latex, however, it is not suitable, because the creaming velocity in latex is very low, due to the small particle size and the slight difference between the specific weight of rubber and that of serum.

3. After increasing times t , the change in concentration c can be determined in a plane O lying h cm. below the surface of the liquid, or corresponding values of h and c can be determined at a single value of the time t . The change in concentration in this plane is caused exclusively by the disappearance of the particles with a diameter larger than D , which have been displaced over the distance h in the time t . The concentration of particles with a diameter smaller than D in the plane O remains the same. From this it follows that, in contrast to methods 1 and 2, the figures obtained furnish immediately the desired values for the weight-distribution curve $V(D)$. If the concentration of the suspension is originally C_0 , and after a time t has become C_{ht} at a height h , the percentage by weight of particles with a diameter smaller than D is $V(D) = C_{ht}/C_0 \cdots (2)$. The value of D for the corresponding values of h and t can be calculated from Stokes' law.

Experimental methods based on this principle are the hydrometer method of Casagrande¹², the *Tauchwagenmethode* of Berg¹³, and the pipette method of Andreassen².

The hydrometer method, in which the change of concentration of the liquid at certain depths is measured by determining the specific gravity with the help of a hydrometer, cannot be used for a suspension which creams with a low velocity of the particles, since the length of the hydrometer cylinder immersed is much too great compared with the height of rise of the smaller particles. This objection is lacking in the *Tauchwagenmethode*, since in that case small glass bulbs of accurately determined specific gravity are introduced into the liquid. However, since the construction and careful calibration of a series of these bulbs are laborious, and in a nontransparent and creaming liquid like latex the method would probably also present difficulties, the choice fell on the pipette method.

In this method, which was originally proposed by Robinson¹⁴, but further developed and rendered accurate by Andreassen¹⁵, samples of the liquid are taken by means of a pipette at a height h below the surface after increasing times, and the concentration in that layer of liquid is determined by analysis. In the original apparatus the sedimentation height was 20 cm., but in the investigation of settling suspensions Heikel, Vinther and Lasson¹⁶ used an apparatus

with a sedimentation height of only 20 mm. These authors ascertained that when the rate of drawing out the sample was slow (about 10 cc. in 4 min.), the sample drawn out was actually taken from an almost horizontal layer of liquid.

b. Description of the apparatus.

Since the rubber particles rise instead of sinking, a height of rise of 20 mm. above the bottom of the vessel was taken as the most suitable measure of the creaming. For the determination of a weight-distribution curve, four to six samples must be taken, while each sample must amount to at least four or five cc., to be able to make an accurate determination, considering the very low concentration of the latex used. If all the samples are taken from a single vessel, it may be assumed that half this amount of liquid of 6×5 cc. = 30 cc., is removed from the 20 mm. column of liquid in question. The volume of the samples, however, must be only a small fraction of this column, since otherwise the measurement becomes inaccurate. To solve this difficulty all the samples were not taken from one vessel, but several vessels were used, and from each vessel a sample was taken only twice, with an interval of several days.

Figure 6 shows the apparatus used. A frame, which is constructed partly of sheet aluminum and partly of plywood, has room for two rows of five vessels. The whole is suspended in a water-bath in such a way that the level of the bath lies slightly below the top of the vessels. The bottoms of the vessels are made accurately flat, and they are closed by a glass plate with a hole in it. The pipette for drawing out the samples is inserted through this hole until its lower end rests on the bottom of the vessel. The capillary stem is fused together at the lower end, which is ground flat, but at exactly 20 mm. from the end two lateral openings with a diameter of about 0.3 mm. are made. If a sample is drawn twice out of each vessel, five points on the distribution curves of two latices can be determined in duplicate with this apparatus.

The vessels were filled with latex which had previously been brought to the temperature of determination. A uniform speed of suction was obtained by connecting the pipette to a very thin drawn-out capillary, which was connected to a slowly emptying leveling bottle.

To avoid convection currents, the vessel must be kept at constant temperature. An arrangement in which temperature fluctuations are practically excluded was found by placing a covered water-bath in a room with a practically constant temperature of 30° C. Over a period of several days only very slow temperature fluctuations of 0.1–0.2° C were observed.

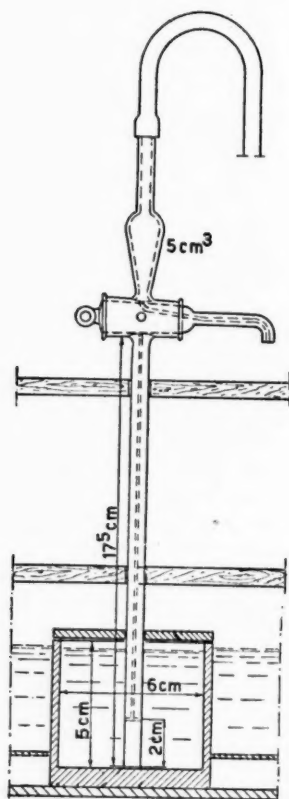
c. The influence of the factor A.

It has already been explained that the percentage by weight of the particles with diameter smaller than D is:

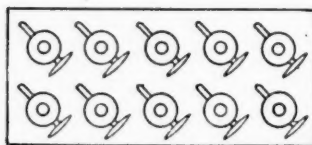
$$V(D) = C_{ht}/C_0 \quad (2)$$

The value of D for the corresponding values of h and t is calculated as follows. From Stokes' law:

$$r = \sqrt{\frac{9}{2g} \frac{\Delta h}{\Delta t} \frac{\eta}{d - d_{v1}}}$$



a. Cross-section of a creaming vessel with pipette.



b. View of the apparatus from above,

FIG. 6.—Apparatus for dispersoid analysis of Hevea latex.

Substituting in this:

$r = \frac{1}{2}D$ in μ

height of rise $\Delta h = -2.0$ cm.

creaming time Δt in hours

d_{v1} = specific gravity of the latex at a height of 2.0 cm.

η = viscosity of the latex at 2.0 cm. height in poises, the formula becomes:

$$D = 2.10^4 \sqrt{\frac{9 \cdot 2.0}{2.981 \cdot 3600t} \frac{\pi}{d_{v1} - d}} = \sqrt{\frac{1.02 \cdot 10^3}{t} \frac{\eta}{d_{v1} - d}} \text{ microns} \quad (3)$$

With the help of formula (3) the relation is calculated between the particle diameter D and the creaming time t at different values of A . This relation is represented graphically in Figure 7. From the parabolic form of these curves

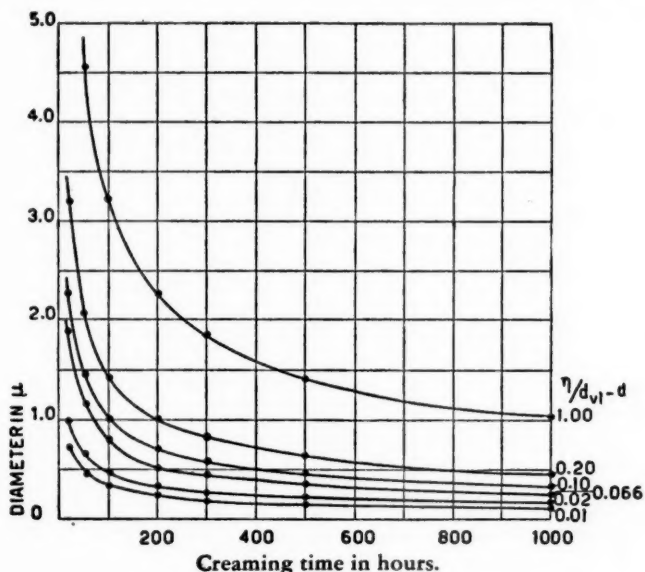


FIG. 7.—Relation between diameter and creaming time in hours for a height of rise of 2.0 cm. at different values of $\frac{\eta}{d_{v1} - d} = A$.

it follows that the larger particles rise through the distance of 2.0 cm. here assumed in a short time. Below a certain diameter, however, the creaming time decreases very rapidly, and the value for the smallest particle diameter which is still measurable is determined chiefly by the factor A , and scarcely at all by the time of rising. With a maximum creaming time of 14 days and a still measurable diameter of about 0.5μ , therefore, A must be smaller than 0.10, according to Figure 7. It has already been calculated that for latex with a rubber content of about 10 per cent, at 20°C , $A = 0.18$. At a lower concentration of the latex the viscosity becomes lower and thus the value of A smaller. It is, however, impossible to go lower in concentration than a rubber content of about 5 per cent, since it would otherwise be difficult to make an accurate de-

termination of the rubber content in samples of 4 to 5 cc. At that concentration, however, the value of A is not yet below the given limit.

A study was therefore made of the influence of an increase in temperature on the magnitude of the factor. This is given in Table III.

TABLE III
INFLUENCE OF THE TEMPERATURE ON THE FACTOR A
OF AN APPROXIMATELY 5% LATEX

Temp. (° C)	d_{v1}	d	$d_{v1} - d$	$\eta \times 10^2$ in poises	A
1	1.004	0.925	0.079	2.1	0.27
20	1.002	0.912	0.090	1.2	0.13
30	0.999	0.907	0.092	1.0	0.11
40	0.994	0.903	0.091	0.8	0.09
50	0.992	0.900	0.092	0.7	0.08

The values for the specific weight of the rubber are taken from an investigation by van Rossem and Lotichius¹⁷. The value given for 30° C is in good agreement with the value for the specific weight of the rubber particles in latex found by other investigators by extrapolation of the specific weight of latices with increasing content of rubber. According to this latter method de Vries¹⁸ found 0.913, Scholz and Klotz¹⁹ 0.901, Rhodes²⁰ 0.9064, and van Gils²¹ 0.9042. The values of d_{v1} for different temperatures are calculated from the specific weights of water and rubber. The difference $d_{v1} - d$ is practically constant for the temperature range 20–50° C. Due to the rapid fall in viscosity with increasing temperature, however, A falls very rapidly, and at 50° C reaches a value of about 0.08. In practice, however, we could not go higher than about 30° C, since a higher temperature was difficult to maintain under the given circumstances.

At 30° C, however, the value of the factor was 0.11, so that other means had to be sought to lower it still further. The only way in which this could be done was by increasing the specific weight of the latex d_{v1} for example, by dissolving salts in it. Such a method can, however, be employed only if the latex does not coagulate as a result of the high concentration of salt; moreover the viscosity of the salt solution must be low; otherwise the desired effect is nullified.

A concentrated solution of 30 to 40 per cent was made of the salt to be investigated, and a calculated amount of this was added to latex of such a rubber content that, after mixing, the latex obtained had a content of about 5 per cent rubber and about 20 per cent salt. It was found that alkali hydroxides and carbonates at this concentration caused flocculation. Moreover the viscosity of these solutions was too high. It is stated in the literature that solutions of various ammonium, potassium, rubidium, and cesium salts, even at high concentrations, have a lower viscosity than water²², so these salts should be particularly suitable for our purpose. In preliminary experiments with ammonium nitrate and ammonium bromide, however, it was found that latex flocculated with these salts also. Varying results were obtained with sodium chloride. To obtain a sodium chloride concentration of 20 per cent in latex, powdered sodium chloride, previously moistened, had to be added to the latex. This succeeded with ordinary latex, but fractionated latices were flocculated.

The addition of a stabilizer to the latex also failed to prevent this flocculation. Peregál, a fat acid derivative, was used. This is not an iogene, but, due to the presence of many solvating groups in the molecule, it has the char-

acter of a soap²³. The use of this substance as a stabilizer of fresh latex has been carefully investigated by the present author²⁴. It was found that latex to which Peregal has been added can no longer be made to coagulate by the addition of acid. On the basis of this experience an attempt was made to obtain an increase in the specific gravity of latex by adding to latex which had been stabilized with about 0.7 per cent of Peregal, sulfuric acid in the form of a solution of 60 per cent by weight. In this way we actually succeeded in obtaining completely stable latices which contained about 5 per cent of rubber and 25–50 per cent by weight of sulfuric acid. On coagulation of this latex a rubber is obtained which is somewhat more plastic than ordinary rubber, but shows no further apparent deviations. An increase of the content of sulfuric acid above about 25 per cent was of no value for our purpose, since the factor A no longer decreased, because of the increase in the viscosity.

Since in performing the analysis the relation must be accurately known between the rubber content of the latex and the viscosity and specific gravity at the prevailing temperature of 29.0° C, this was determined in advance. The values found are included in Table IV, which also gives the composition of the latices. The relation between the rubber content and the viscosity of the latex or the specific weight was plotted graphically, and was found to be linear in this range. From the calculated values of A in the last column of Table IV,

TABLE IV
SPECIFIC GRAVITY AND VISCOSITY OF LATICES WITH 25 PER CENT
SULFURIC ACID AND INCREASING DRY RUBBER CONTENT AT 29° C

Composition of the liquid					Dry rubber content in %	Specific gravity	Viscosity in c.p.	$A = \frac{\eta}{d_{v1} - d}$
Total vol. (cc.)	cc. of 17% latex	cc. of 20% Peregal	cc. of water	cc. of 60% sulfuric acid				
water	—	—	—	—	—	0.996	0.818	—
61.0	0	1.5	39.5	20.0	0	1.163	1.43	—
61.0	4.0	1.5	35.5	20.0	1.12	1.162	1.50	0.059
61.0	8.0	1.5	31.5	20.0	2.23	1.161	1.57	0.062
61.0	12.0	1.5	27.5	20.0	3.35	1.159	1.66	0.066
61.0	16.0	1.5	23.5	20.0	4.46	1.158	1.72	0.069

it may be seen that these values under the chosen conditions fulfil the required condition, and that the analysis of particles with a diameter of 0.4 to 0.5 μ in a creaming time of less than about 14 days is now possible.

d. The analysis.

From latex sample A, a latex was made in the way indicated which contained 4–5 per cent of rubber and 25 per cent of sulfuric acid. After this had taken on a temperature of 29.0° C five vessels were filled with 100 cc. After the apparatus had been prepared, samples were drawn out at intervals chosen by reference to the curve in Figure 7. The samples of each latex were taken from two vessels each time. They were run into weighed weighing bottles, weighed, and then rinsed over into porcelain dishes with water. After several drops of methyl red had been added, a small excess of 10 per cent sodium hydroxide was added, and the mixture was afterwards acidified with 10 per cent acetic acid. During this treatment the latex flocculated. The liquid was then evaporated on the water-bath to a volume of about 10 cc., and filtered. The rubber coagulum on the filter and in the dish was collected, pressed out to a thin membrane with the fingers, and thoroughly washed to free it of salt.

For this purpose the coagulum in a porcelain dish was extracted with water for half an hour on the water bath. The water was poured away, and the operation repeated. To remove coagulated components other than rubber, the coagulum was then treated twice more with 5 per cent ammonia, and once with water. If during evaporation and washing care was not taken that the coagulum was always well covered with liquid, it became sticky and difficult to handle. After this washing process the coagulum was cut into small pieces and dried to constant weight at 70° C on a weighed watch glass. The rubber consisting of the finest particles had a particularly great tendency to become sticky during this drying, thus retarding the drying, which then took 5 to 8 hours. It was ascertained that this stickiness does not appreciably affect the weight of the rubber and thus introduces no difficulty in the analysis. As a check on the washing of the coagulum, an ash determination was performed, and an ash content of 0.36 per cent was found, so the purity of the rubber was sufficient for our purpose.

Table V gives the results of the dispersoidal analysis of latex A. The first column gives the time in hours; the second and third give the results of the samples taken in duplicate with the calculated average values. From the values obtained, $V(D)$ in percentage and D in microns can be calculated with the help of formulas (2) and (3).

TABLE V
SEDIMENTATION ANALYSIS OF LATEX A

Time in hours	Rubber content in %			η in c.p.	d_{v1}	$d_{v1} - d$	D in μ	$V(D)$ in %
	1	2	average					
0	3.97	3.98	3.98	1.75	1.161	0.254	—	—
18	4.05	4.01	4.03	1.75	1.161	0.254	1.97	100
42	3.22	3.29	3.26	1.69	1.162	0.255	1.26	82
90	2.29	2.39	2.34	1.62	1.162	0.255	0.85	59
162	1.49	1.43	1.46	1.55	1.163	0.256	0.62	37
210	1.24	1.27	1.26	1.54	1.163	0.256	0.54	32
260	1.08	1.13	1.11	1.53	1.163	0.256	0.48	28

In Figure 8 the weight-distribution curve of latex A is plotted, while in Figure 9 the curves are given for a number of fractions of very varied particle size obtained from it (see Figures 1 to 4). The shape of the curves for a diameter smaller than about 0.4μ , which was not determined, is extrapolated by approximation and drawn as a dotted line.

e. Comparison of the results of the two methods.

For the sake of comparison in Figure 8 the weight-distribution curve is also plotted as calculated from the photomicrographic dispersoidal analysis. From the shape of the two curves it follows that the largest diameter found by the two methods is about the same, and is equal approximately to 1.8μ . This agreement in results of two entirely different methods may be considered satisfactory. At the same time it may be concluded that, during creaming under these conditions, there is no formation of clusters, but that the particles in the liquid rise separately. The further agreement of the curves is less satisfactory. The distribution curve obtained by the photomicrographic method lies in general higher than the one obtained by sedimentation analysis; the difference between the two methods becomes greater, the smaller the particles. The proportion of particles with a diameter smaller than 0.4μ is only a few

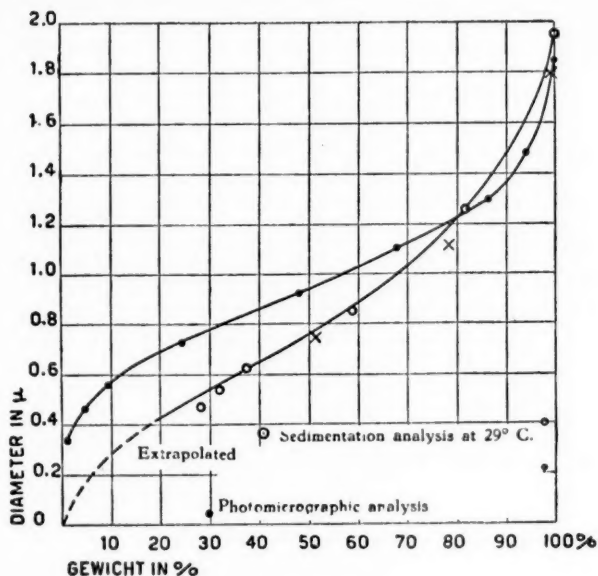


FIG. 8.—Weight-distribution curve of latex A, determined by creaming analysis.

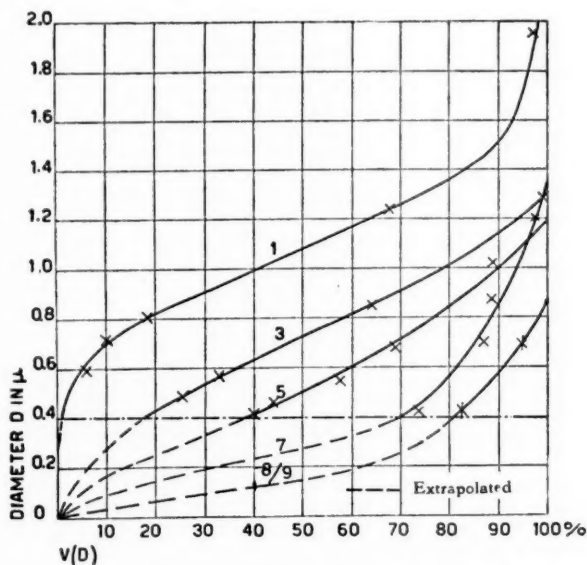


FIG. 9.—Weight-distribution curves of the fractions of latex A, determined by creaming analysis.

per cent by one method, but about 20 per cent by the other. These differences must be explained by the fact that in the photomicrographic method particles with a diameter of less than about 0.35μ could not be determined, while in the sedimentation analysis the percentage by weight of particles whose diameter is too small to be determined directly is nevertheless accurately known. Also because of the fact that in the latter method the weight-distribution curve is found directly, and need not be calculated from the number of particles, as in the photomicrographic method, it follows that sedimentation analysis is much to be preferred. Andreasen estimates the errors of the pipette method as originally given by him at 2-5 per cent. In the method described here the errors are not in general larger. From the duplicate values of the rubber content found, it is evident that the deviations from the average value do not generally amount to more than 2-3 per cent, while from Formula (3) it follows that a small error in the determination of η or $d_{v1} - d$ has only a slight effect on the values of D .

This dispersoidal analysis of Hevea latex by a modified form of sedimentation analysis has advantages over photomicrographic analysis because it is accurate and less elaborate, requires only simple apparatus, and is excellently suited for series of investigations. The principle of increasing the creaming or sedimentation velocity of small particles by the addition of other substances, combined with the measurement of the change in concentration within only a small difference in height, may also be applied to the determination of distribution curves of other natural or synthetic finely dispersed latices. The choice of stabilizer and of the substance to be added to bring the value of the factor $\eta/d_{v1} - d$ of the suspension to the desired value should, however, be adapted in each case to the requirements of the suspension under consideration.

SUMMARY

For the purpose of determining the weight-distribution curve of the rubber particles in *Hevea* latex according to their diameter, two methods were employed, namely, photomicrographic dispersoidal analysis and sedimentation analysis. In addition to the fact, that the first method is very laborious, its precision does not prove to be high, mainly because a significant percentage of the particles is too small to be determined microscopically in the visible spectrum. Sedimentation analysis with the help of a modified pipette method according to Andreasen was found, however, to be very suitable for the purpose. By an accurate regulation of the viscosity, specific gravity and temperature of the suspension it became possible to determine the weight-distribution curve of latex to a diameter of about 0.4μ within a creaming time of 10 to 14 days, while the total percentage of still smaller particles was also determined at the same time. This method is accurate, not too laborious, and lends itself very well to a series of investigations.

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NATURAL COAGULATION OF *HEVEA* LATEX *

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INTRODUCTION

Natural coagulation has been of interest during the last forty years. As no satisfactory explanation could be given for this phenomenon, it still continues to attract attention. It is now accepted that the instability of latex is caused by certain changes in the chemical composition of the latex components, but it is still an open question what those chemical changes are, and by what agents they are caused. The explanations of the changes have given rise to two rival theories, the so-called enzyme theory, and the bacteria theory.

The first, supported by Whitby¹, Campbell², Barrowcliff³, Stamberger⁴, Stevens⁵, and Paton⁶, imputes the direct cause of the natural coagulation to the activity of an (unidentified) enzyme. They admit that, under the influence of bacteria, acids are formed in the latex during the process of natural coagulation, but they consider these acids to have only an activating influence on the enzyme.

Gorter and Swart,⁷ Eaton,⁸ Denier and Vernet⁹, Spoon¹⁰, Belgrave¹¹, De Vries and Beumée-Nieuwland¹², Bobilioff¹³, Corbet¹⁴, Van Dillen and Heubel¹⁵, and most of the modern investigators support the bacteria theory, postulated by Eaton and Grantham¹⁶. According to this theory the acids produced by bacterial action are the direct cause of the natural coagulation.

It is beyond the scope of this paper to make a critical examination of these theories. It has been amply done in the publications of Belgrave and of Corbet¹⁴, whose explanations give but poor support to the enzyme theory. A major objection to the bacteria theory was that the bacterial production of acids proved to be insufficient to attain the pH value necessary for normal coagulation ($pH = 5.0 \pm 0.2$). In this connection reference should be made to the papers of Hauser and Scholz¹⁷, Van Harpen¹⁸, Paton (*loc. cit.*), Stevens¹⁹, and Stamberger⁴. This experimental fact is a direct contradiction of the experimental results of Spoon¹⁰, Ultée and Van Dillen²⁰, and Bobilioff¹³. These investigators certainly found a considerable decrease of the pH value in the coagulation process. Spoon was able to show that the bacteria produced a quantity of acid just corresponding with the quantity of acetic acid required for a normal coagulation. It may be true that Spoon, Ultée and Van Dillen, and Bobilioff, not possessing the modern precision apparatus, were more handicapped in making exact observations than the modern experimenters. Another important fact is that in a complicated mixture as *Hevea* latex, bacteria may produce also alkalies beside acids. About this subject the following may be communicated.

It was thought that two kinds of bacteria were present, namely, anaerobic bacteria able to accelerate the coagulation by transforming sugars into acids, and aerobic bacteria repressing the coagulation by hydrolyzing proteins to

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 22, No. 5, pages 274-282, February 1947.

give alkaline products²¹. With regard to *Hevea* latex, Whitby²² drew attention to the work of Kendall²³ which indicated that "fermentation takes precedence over putrefaction". This means that, if both sugars and proteins are present, the bacteria affect the sugars first (causing "fermentation") and afterwards the proteins producing putrefaction products. It is an open question whether this is due to a preference for sugars above proteins or if this can be explained on the ground that fermentation processes proceed more rapidly than putrefaction processes. Naturally, a lot depends on the strains of bacteria present. During the fermentation process acids are formed, whereas nitrogenous, alkaline substances are produced by the bacteriological cleavage of proteins. This possibly explains the observation that, in the process of spontaneous coagulation, putrefaction is suppressed by extra quantities of sugar added to the latex (cf. Eaton and Grantham¹⁶ and Gorter and Swart⁷). The experiments of the author (unpublished) proved that the nonrubber constituents of latices from different clones occur in strongly divergent quantities. This varying composition of different latices explains why the natural coagulation is sometimes completed and sometimes not completed within 24 hours¹⁰. Thus, in a sample of latex to which an excessive quantity of sugars and quebrachitol is added, not only are more acids formed, but it is also possible that the production of alkaline substances starts at a later period than in a sample containing relatively much less sugars and quebrachitol. Perhaps this partly explains the strongly divergent results on the one hand of Spoon, Ultée and Van Dillen, and Bobiloeff, and on the other of Hauser and Scholz, Van Harpen, Stevens, and Stamberger.

In addition to the enzyme and bacteria theories, the following opinions are worthy of mention. De Vries and Beumée-Nieuwland¹², considering the flocculation of the rubber particles as a result of the action of acids which are produced by bacteria, attributed the change of the flocculate into a coagulum to an enzyme activity. According to Van Harpen¹⁸ certain compounds, the so-called hydratants, are responsible for the natural coagulation. Van Harpen's hydratant-acid occurring in latex as a natural component was, however, identified as a mixture of higher fat acids and proteins²⁴.

The interesting experiments of Van Gils²⁵ shed a new light on the question of coagulation. This investigator stated that calcium and magnesium salts on the higher fat acids have a flocculating action on oil-water emulsions, and that therefore natural coagulation should be attributed to those salts, which are slowly formed in the latex²⁶. The acceleration of natural coagulation, caused by different soluble calcium salts, and too often put forward as an argument favorable to the enzyme theory³ now appears more understandable.

Few data exist in literature concerning the nature of the changes in the chemical composition of latex by bacterial activity. On this subject Gorter and Swart⁷ performed important work. From latex to which sugar was added they were able to isolate, after coagulation, acetic acid, lactic acid, and succinic acid, and they observed the formation of carbon dioxide. The formation of lactic acid in the coagulation of latex to which sugars were added beforehand was also observed by Eaton⁸. Moreover, the latter showed alcohol, traces of acetone, and formic acid to be present in the coagulation product. Spoon¹⁰, Ultée and Van Dillen²⁰, and Bobiloeff¹³ also detected the formation of acids, but they could identify only carbon dioxide. Schrieke²⁷, finally, could not detect any acid but carbonic acid.

In an attempt to elucidate the problem the present analytical investigation was made by following the changes of the chemical constitution of the latex gradually taking place during the process of natural coagulation. In this

paper the changes of the yields, the saponification value, and the acid value of the nonrubber ether-soluble substances of the latex are recorded. Besides this, one series of analyses was made on the change of the nonvolatile acid-content of the ether-solubles.

All operations were conducted in such a way that in the morning as early as possible, one liter of latex was gathered from the cups and poured into a stoppered cylinder, from which 100 cc. of latex was immediately pipetted. Such samples for analysis were taken every two hours until spontaneous coagulation took place. Exclusively latex from clone Tjirandji 1 from the Experimental Garden Tjiomas near Buitenzog (Java) was used.

CHANGES IN YIELD OF ETHER-SOLUBLES

The pipetted quantity of latex was added to 750 cc. of 96 per cent alcohol with vigorous mechanical stirring. The rubber coagulum formed was pressed by hand and, without washing, very thinly creped on the rolling mills. The crepe was then extracted continuously during 10 hours and the extract obtained evaporated to dryness under reduced pressure in a carbon dioxide atmosphere at about 45° C. The buttery residue was taken up with 10–15 cc. of absolute alcohol and the solvent evaporated again *in vacuo*. This operation was repeated at least three times to obtain an absolutely dry product. The residue finally obtained was dissolved in ether, filtered, evaporated to dryness, and dried in a vacuum desiccator to constant weight²⁸.

The results obtained from three different samples of latex are given in the table and plotted in Figure 1. It appears that the yield rapidly decreases in

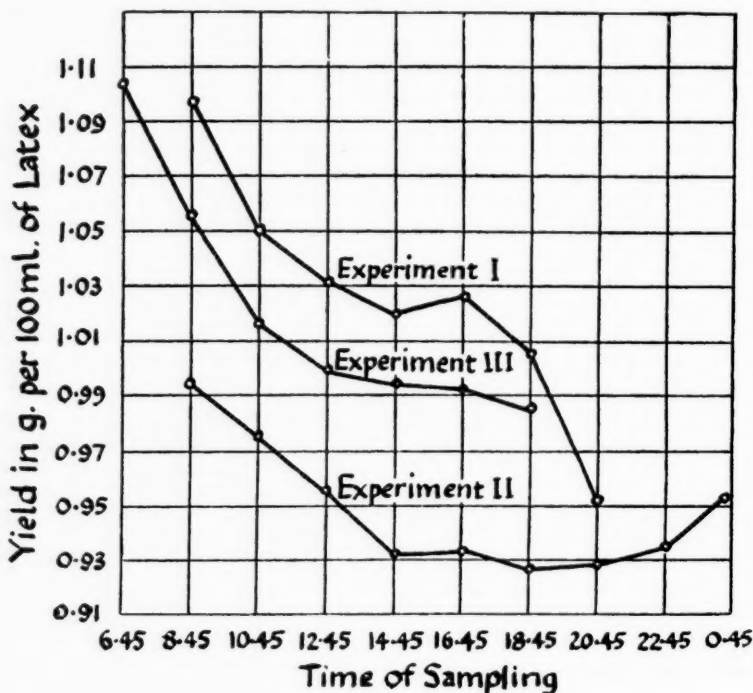


FIG. 1.

the first eight hours of the process of coagulation; then, after a short period when it remains practically unchanged, the yield finally falls (Experiment I) or rises (Experiment II). The final fall in Experiment I is not normal and must be ascribed to the lumps formed at the end of the process of coagulation. A considerable quantity of the ether-solubles is thus precipitated together with the lumps, and consequently is not found in the pipetted sample. For that reason a cylinder instead of a pipette was used in Experiment II, from which, consequently, relatively smaller yield figures are obtained than in Experiment I. This is, however, of no importance, since the analytical figures are only comparative. The changes in yield will be discussed in a later section.

CHANGES IN SAPONIFICATION VALUE OF ETHER-SOLUBLES

As, in general, no more than about one gram of ether-soluble substances can be obtained from the 100 cc. latex-samples, only 60 to 100 mg. of the ether-solubles was used for the determination of the saponification numbers. Duplicate determinations were performed.

For the sake of completeness the method of analysis may be given now.

Exactly 5 cc. of a 0.2 *N* alcoholic potash-solution is added to 60–100 mg. of ether-solubles, weighed in a 50-cc. Erlenmeyer flask with ground joint. The mixture is then gently boiled under a reflux on a steam bath for half an hour. Exactly the same quantity of the alcoholic KOH is similarly boiled as a blank. After saponification is complete, the excess KOH is back titrated with 0.1 *N* HCl by a microburette. The saponification value (S.V.) is found with the formula: $S.V. = \frac{56.11(p - q)}{g} n$, in which *p* = cc. of HCl required in the blank;

q = cc. HCl required after saponification of the ether-solubles; *g* = weight of the ether-solubles in grams; *n* = normality of HCl used, and 56.11 = molecular weight of KOH.

In the saponification number thus calculated, the quantity of nonfat acids present in the ether-solubles, *i.e.*, phosphoric acid, dicarbonic acids, hydroxy acids, resin acids, etc., are also included. As a matter of fact, the ether-solubles contain considerable quantities of phospholipides, easily forming phosphoric acid or its glycerol esters²⁹.

As will be seen from the figures given in the table and which are plotted in Figure 2, the course of the saponification numbers during the process of natural coagulation is remarkable. At first a rapid drop, reaching a minimum 8 to 12 hours after the commencement of latex-tapping, afterwards a sharp rise. A possible explanation is given below.

TABLE
CHANGES OF YIELD, SAPONIFICATION VALUE, AND ACID NUMBER OF
ETHER-SOLUBLES DURING THE PROCESS OF NATURAL COAGULATION

Time of sampling	Yield in g. per 100 cc. latex			Saponification number		Acid number	
	Expt. I	Expt. II	Expt. III	Expt. II	Expt. III	Expt. I	Expt. III
6.45	—	—	1.1062	—	153.5	—	29.1
8.45	1.0984	0.9925	1.0548	144.2	143.9	22.3	29.1
10.45	1.0496	0.9778	1.0170	137.9	139.8	17.1	20.1
12.45	1.0311	0.9583	1.0034	136.7	132.3	18.2	20.5
14.45	1.0223	0.9303	0.9989	130.5	121.2	17.0	20.0
16.45	1.0280	0.9320	0.9956	131.6	120.6	22.0	19.3
18.45	1.0074	0.9270	0.9879	127.3	144.4	18.0	43.7
20.45	0.9515	0.9288	coag.	131.1	coag.	18.1	coag.
22.45	coag.	0.9347		136.3		coag.	
0.30		0.9514		147.3			

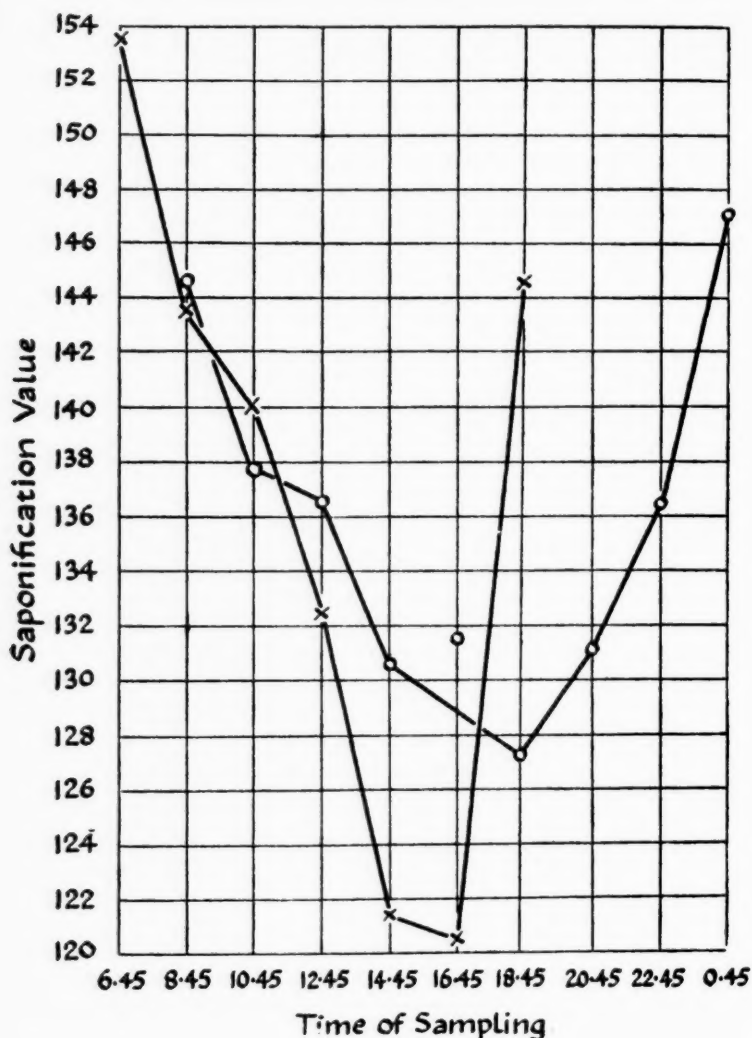


FIG. 2.

CHANGES IN THE ACID NUMBER OF ETHER-SOLUBLES

For the same reason as mentioned in the foregoing section, not more than 60 to 100 mg. of ether-solubles was used for each determination of the acid number.

If the hypothesis of Van Gils²⁶ is correct, all fat acids occurring in a free state in the latex are immediately transformed into their ether-insoluble magnesium or calcium salts and are thus eliminated from the analysis. Consequently, in every sample an acid number = 0 should have been found. That this could not be affirmed experimentally must probably be due to partial hydrolysis of the fats during and after extraction. Such saponification ap-

parently cannot be prevented in the method of separating the ether-solubles from latex.

Attention may be drawn to the two extreme figures in Experiment III, which are remarkable when compared with other figures in the Table, which are almost equal. This fact will be discussed later.

THE FAT ACID CONTENT

In addition to the above, attention was paid to the change of the fat acid content of the ether-solubles during the process of natural coagulation. The acid content was determined by the method of Fahrion³⁰, according to which, however, all other ether-soluble acids present (hydroxy acids, dicarbonic acids, resin acids, etc.) are isolated and weighed. It is found that the acid content shows a decrease in the first hours of the coagulation process.

DISCUSSION OF RESULTS

To explain the experimental data, it should be kept in mind that the ether-soluble nonrubber components of the latex consist among other products of fats (glycerides), phospholipides (lecithins, cephalins), waxes, sterolines, etc., *e.g.*, products which, on saponifying, form several compounds not soluble in ether, such as glycerol, phosphoric acid or its glycerol esters, choline, colamine, glucose, etc. As, undoubtedly, saponification takes place during the process of natural coagulation, the quantity of the ether-solubles consequently must decrease gradually in the course of that process. Theoretically speaking, such a decrease continues as long as unsaponified fats, phospholipides, etc., remain in the spontaneously coagulating latex.

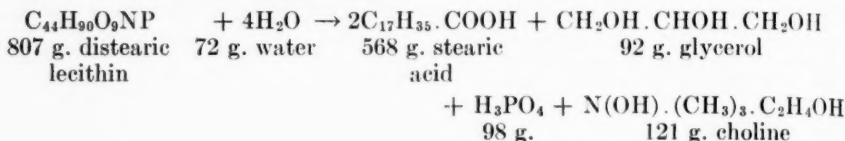
Viewed in this light the experimentally found decrease of the yield figures in the first eight hours of the process is quite comprehensible. However, in the period thereafter the yields apparently remain almost constant, which is seemingly in contradiction to the above theoretical considerations, for it is improbable that the fats, phospholipides, etc., are all saponified eight hours after tapping. If this were true the saponification and acid numbers should be about equal. The experimental results show, on the contrary, that saponification and acid numbers differ greatly from each other during the whole process of natural coagulation.

It is believed, therefore, that the loss of yield of fats, phospholipides, etc., is accompanied by an increase in some other ether-soluble compounds newly formed, probably by the action of phosphoric acid or its strong acid-reacting glycerol esters on the magnesium and calcium salts of the fat acids, thus reproducing the free fat acids. This surmise finds confirmation in the facts that (1) the saponification numbers, after having reached a minimum, sharply rise, (2) the acid value (see Experiment III) shows the highest figure just before coagulation takes place. It is further noticed that the moment at which the yield reaches a constant value almost coincides with the moment at which the saponification number reaches its minimum.

As regards the rapid fall of the saponification number in the first 6-10 hours of the coagulation process, this can satisfactorily be explained by the following considerations.

As a matter of fact, the phospholipides and the glycerides are the most important components of the ether-solubles³¹. It is, therefore, necessary to examine in what measure, theoretically speaking, the saponification values of these compounds change when hydrolysis proceeds.

The phospholipides, supposing they consist of distearic-lecithin, saponify according to the following equation:



In consequence of the fact that, of all the saponification products obtained, only stearic acid is soluble in ether, the completely saponified lecithin produces in the adopted method of analysis a saponification number equal to the acid number of two moles of stearic acid, *i.e.*, 197.7.

In the unhydrolyzed state, however, the saponification number of the lecithin amounts to a much higher figure, namely 347.6, which is found according to the formula:

$$\text{S.V.} = \frac{\text{mg. KOH, required for neutralizing 2 moles stearic acid and 1 mole H}_3\text{PO}_4}{\text{molecular weight of lecithin (= 807)}}$$

In other words: hydrolysis of lecithins results in a considerable decrease of the saponification value.

In the case of glycerides, hydrolysis influences only feebly the saponification value, but in the reverse way. A simple calculation demonstrates that in hydrolyzing, for example, 1 mole of glyceryl tristearate, the saponification value increases from about 189 to about 197. As the ether-solubles contain, relatively speaking, more phospholipides than glycerides³¹, this increase may be neglected in regard to the decrease caused by the lecithin saponification, so the decrease of the saponification value of the ether-solubles in the beginning of the coagulation process can be considered completely normal.

Not normal is perhaps the rapid fall of the curves in Figures 1 and 2. Fats and phospholipids in aqueous suspensions do not saponify, generally speaking, so quickly as indicated by the curves. The accelerating factor in the hydrolysis can perhaps be some enzymatic activity and the rapid formation of the magnesium and calcium salts of the fat acids. A confirmation of the latter may be found in the experimental statement that the fat acid content of the ether-solubles decreases during the first hours of coagulation.

EXPLANATION OF NATURAL COAGULATION

From the above the following explanation of the natural coagulation of *Hevea* latex seems to be applicable.

Either by the bacterial action on sugars, quebrachitol, etc., or by the enzymatic or chemical hydrolysis of fats, phospholipides, etc., several acids, including phosphoric acid or its glycerol esters, can be formed in spontaneously coagulating latex. Since many buffering substances are present in the latex, those acids at the beginning of the coagulation process have no influence on the colloid chemical equilibrium. But as soon as the buffering substances are completely attacked by the acids formed, the coagulating action of these acids becomes perceptible or even decisive. Because some of the formed magnesium and calcium salts already influence strongly the colloid chemical balance²⁵, only a small quantity of acid is necessary for causing coagulation. As coagulation does not take place at the moment at which no more ether-insoluble

salts are formed, i.e., the moment at which the saponification value passes its minimum, the salt formation alone must be considered insufficient for causing coagulation.

The observations made by former investigators (see Introduction) find a satisfactory explanation in the theory just outlined. In this connection the experimental statements of Stamberger¹ are most interesting, as they afford valuable support to the present theory. According to Stamberger, namely: (1) several samples of latex did not show any change in pH after coagulation, whereas others showed only a slight (0.2 to 0.3) decrease; (2) no increase in the rate of coagulation was observed with latex samples to which potassium hydroxide-phthalate buffer solution was added. In the light of the outlined theory this observation is quite understandable if one only keeps in mind that the acids formed by hydrolysis of the ether-solubles of the latex, first neutralize the potassium hydroxide; second, produce their magnesium and calcium salts; and third, decrease slightly the pH. In other words, the potassium hydroxide-phthalate buffer does not influence in any way the formation or the quantity of the Mg and Ca salts, and therefore the rate of coagulation is left unchanged. (3) No change of pH was observed in samples to which strong antiseptics (pentachlorophenate) were added. The coagulation took place in the same time as without the addition of antiseptics. This observation may prove that the acids derived from the ether-solubles are formed not by bacterial action but by ordinary hydrolysis-processes whether or not accelerated by enzymes. (4) In studying the effect of other substances on the prevention of coagulation, it was observed that potassium hydroxide was only effective in 0.3 per cent concentration, sodium carbonate and sodium phosphate were totally ineffective, even in concentrations as high as 2 per cent. Oxidizing agents, however, were found to be more effective: sodium perborate and hydrogen peroxide prevented coagulation in concentrations of 1 to 2 per cent. This observation probably indicates that saponification of the acid-forming ether-solubles takes place under the influence of enzymes which are poisoned by ammonia or destroyed by oxidizing agents or strong chemicals. However, as will be demonstrated in another paper on the chemical changes in ammoniated latex, saponification takes place in ammoniated latex as well as in fresh latex. The alkalinity of the ammonia added, therefore, is still of great importance in preventing coagulation.

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ORGANIC ANALYSIS OF HEVEA LATEX. IX. SOME DETAILS OF THE MAIN FRACTIONS *

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INTRODUCTION

As a result of attempts to isolate and identify various groups of organic compounds which occur naturally in Hevea latex, *e.g.*, proteins¹, lecithins², amino acids³, amines and betaines⁴, alkaloids⁵, and fat acids, resin acids, sterols and wax alcohols⁶, the author developed some years ago a general scheme for the systematic analysis of latex⁷. This paper, in completion, contains further details of the first fractions which are obtained on application of the general scheme, and which therefore have been called main fractions. Since it appeared desirable for several reasons⁷ to limit the analytical investigations to latex of one definite Hevea clone, the figures given below apply exclusively to fresh unammoniated latex of clone Tjirandji 1 (Tjir 1) tapped in the Tjiomas experimental garden near Buitenzorg. The recorded percentages are averages of figures obtained from several duplicate estimations.

PREPARATION

The scheme of analysis is given in the large table. The preparation of the main fractions will be clear by the following additional details⁷. As soon as the fresh latex is completely poured out into the alcohol, the rubber coagulum is collected, pressed vigorously by hand, and then thinly creped on the mills without using any wash water. The remaining alcoholic solution is turbid as it contains small particles composed of rubber, proteins, and inorganic compounds, chiefly magnesium ammonium phosphate. This mixture, which is called *Precipitate I*, can easily be isolated by allowing the mass to stand for some time, whereupon the clear alcoholic solution is decanted as far as possible, and the remaining turbid mass is centrifuged. The white centrifuged mixture is washed three times with alcohol and dried in a vacuum desiccator.

The thinly creped coagulum is best extracted in a Soxhlet apparatus, using successively the clear alcoholic solution obtained and distilled water as the extracting liquids. To prevent decomposition of the extracted component, calcium carbonate is added so that phosphoric and other strong acids, formed by hydrolytic processes, are immediately bound in the form of their calcium salts and thus made harmless.

The alcoholic extract obtained after filtration of *Precipitate II* yields a clear solution of a marked yellow or orange color. The latter when distilled in an atmosphere of carbon dioxide under reduced pressure gives the *distillate*, containing mainly the recovered alcohol, besides certain volatile compounds, and the distillation residue which, still containing some alcohol, is a slightly brownish liquid mixed with an orange colored buttery substance. This mix-

* Reprinted from the *Recueil des Travaux Chimiques des Pays-Bas*, Vol. 65, No. 12, pages 919-925, December 1946.

ture when thoroughly shaken with ether in a separatory funnel—if necessary with the addition of a quantity of fresh alcohol—yields the *ether-solubles* and the *water-solubles*, both containing the *solids* mentioned in the scheme. The latter are prepared on the one hand by evaporation of the ether-alcoholic solution to complete dryness, followed by the solution of the residue in pure ether again, and filtration of the insoluble matter; on the other hand by the distillation of the water-alcoholic solution in a vacuum, to remove the alcohol completely, followed by the centrifuging of the distillation residue and by the washing of the centrifuged solids three times with water. In this way a fairly good separation of the *ether-solubles*, *water-solubles*, and *solids* can be accomplished. (Instead of ether, ligroin may be used. In that case, however, since the solids do not dissolve completely in the ligroin nor in the water layer, an extra manipulation, *i.e.*, the filtration or centrifuging of the solids, cannot be avoided.)

The thin crepe, which was successively extracted with alcohol and water, still contains most of the proteins originally present in the latex. For the time being the author disregards the separation of these two main fractions, rubber and proteins, since this has already been done by Midgley, Henne and Renoll⁸ and since, as the other nonprotein nitrogenous substances have already been separated from the rubber hydrocarbon, the protein content may be calculated from the nitrogen content of the extracted rubber (see below).

QUANTITATIVE DATA⁹

FRACTIONS A AND B: THE RUBBER HYDROCARBON AND THE PROTEINS

These two main fractions, as was just pointed out, were not separated from each other. Starting from 100 grams of fresh latex¹⁰, one obtains an average of 38.3 grams of this mixture which contains 0.10 per cent acetone extract, 0.48 per cent nitrogen, 0.40 per cent ash, and 0.12 mg. of copper per 100 grams of rubber¹¹.

Thus, in 100 grams of latex $0.48/100 \times 38.3 \times 6.25$ g. or approximately 1.15 grams of proteins are present. It should be mentioned that this amount does not represent the total quantity of proteins present in the latex, since *Precipitate I* also contains some proteins, whereas the solids appeared to contain prolamines, among other substances (see below).

The pure rubber content, calculated from the figures mentioned above, amounts approximately to:

$$38.3 - \left(1.15 + \frac{0.10 + 0.40}{100} \times 38.3 \right) = 37.0\%$$

These calculations do not, however, express exactly the quantities of the main fractions really present in the latex. The mistakes made consist mainly (1) in the assumption that the proteins are the only nitrogen-containing compounds present in the extracted crepe, and (2) in the subtraction of the amount of ash from the total weight of A + B. In this connection the following theoretical considerations may be of interest.

Assuming that the ash of the extracted rubber consists exclusively of $\text{Mg}_2\text{P}_2\text{O}_7$ ($M = 222$)¹², the insoluble inorganic salts originally present in the alcohol and water-extracted crepe are composed of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ($M = 245$). Thus the quantity of ash found in 38.3 grams of crepe, *i.e.*, $0.4/100 \times 38.3$

= 0.1532 gram, represents $0.1532 \times \frac{2 \times 245}{222} = 0.3381$ gram of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, corresponding to $\frac{14}{245} \times 0.3381$ gram of nitrogen, or $\frac{100}{38.3} \times \frac{14}{245} \times 0.3381 = 0.05$ per cent nitrogen, when calculated on the basis of the dry crepe.

Hence the quantity of proteins present in 100 grams of latex amounts, not to 1.15 grams, but to: $\frac{0.48}{100} - 0.05 \times 6.25 \times 38.3 = 1.03$ grams.

Consequently in the calculation of the percentage of pure rubber hydrocarbon, the following correction should be made:

$$38.3 - \left[1.03 + \left(0.1532 \times \frac{2 \times 245}{222} \right) + \left(\frac{0.10}{100} \times 38.3 \right) \right] = 36.89$$

instead of 37.0.

Apparently extraction of the thin crepe with both alcohol and water does not remove all nonrubber components. Besides the proteins and certain inorganic matter, a small amount of a brownish, tacky product, having a resemblance to "caoutchol"¹³, is still present in the crepe, as is proved by the acetone extraction. The quantity of this product, which never exceeds 40 mg. per 100 grams of latex, is, however, of no great importance.

FRACTION C: THE WATER-SOLUBLES

The yield of the water-soluble components collected, when dried in a vacuum desiccator to constant weight, amounts to 3.2 per cent.

To obtain an impression of its chemical constitution, this complex mixture was subjected to the *lead precipitation procedure*, which involves the addition of a 25 per cent lead acetate solution to the water-solubles in acetic acid and in ammoniacal medium, respectively. These two precipitates, as well as the filtrate (the latter obtained after the removal of the precipitates), were worked up by the usual decomposition procedure with hydrogen sulfide, whereupon the lead sulfide was filtered out and the filtrate evaporated in a vacuum to dryness. In this way the subfractions, *a*, *b*, and *c*, were obtained:

- (a) The *acid lead acetate precipitate* (yield 0.08 per cent) appears to contain strong acids, such as free phosphoric acid and glycerol- and inositol-phosphoric acids. One gram of this subfraction is neutralized, on the average, by about 270 mg. of KOH.
- (b) The *ammoniacal lead acetate precipitate* (yield 0.09 per cent) contains, among other substances, some nonreducing sugars, yielding pentoses, methylpentoses, and hexoses on hydrolysis, besides an organic magnesium salt which crystallizes in lustrous hexagonal plates.
- (c) The *filtrate* (yield 3.0 per cent) still contains a great variety of chemical individuals, *e.g.*, quebrachitol, other inositol derivatives, the hexagonal plates mentioned under (b), amines, amides, amino acids, and other organic and inorganic compounds. The ash content of this filtrate amounts to 7.9 per cent. The author has already described the isolation and analysis of mixtures of amino acids³ and of amines⁴. It is now found that the mixture which is separated from the filtrate by the method of Neuberg and Kerb¹⁴ and which contains amines, amino acids, and amides (asparagine, glutamine), can be obtained in 0.26–0.28 per cent yield, calculated on the basis of fresh latex.

FRACTION D: THE ETHER-SOLUBLES

This main fraction is obtained in a 0.92–1.1 per cent yield, depending on the moment at which the latex sample is added to the alcohol¹⁵.

The ether-solubles¹⁶ appear to consist of approximately 45 per cent fats (glycerides), 33 per cent lecithins, and 22 per cent cephalins; these figures were determined by pouring the dry and concentrated ethereal solution into an excess of pure acetone. The precipitate, containing a mixture of lecithins and cephalins, is then extracted with absolute alcohol in which the cephalins are almost insoluble¹⁷.

The following characteristics of the dried ether-solubles may be recorded. It should be remarked that some of these characteristics, *e.g.*, the saponification value, the organic acid content, the glycerol content, etc., also depend on the moment at which the saponification processes are suppressed by the alcohol added.

Organic acids (Fahrion)	60.1%
Glycerol (Shukoff-Schestakow)	8.1%
Unsaponifiables (Fahrion)	22.7%

SUMMARY OF THE EXPERIMENTAL RESULTS OBTAINED

Main fractions	Yield in percentage of latex	Characteristics (contents are expressed in percentage of the main fractions concerned)
A+B rubber hydrocarbon + proteins	38.3	Acetone extract = 0.10%; nitrogen = 0.48%; ash = 0.40%; copper = 0.12 mc. per 100 g. of rubber
A rubber hydrocarbon	36.9	Estimated by calculation
B proteins	1.03	Estimated by calculation
C water-solubles	3.2	Acid Pb acetate ppt. = 2.5%; ammoniacal Pb acetate ppt. = 2.7%; filtrate = 94.8%; amines, amides, amino acids = 8.4%; ash: 7.9% of the filtrate
D ether-solubles	0.9–1.1	Fat (glycerides) = 45%; lecithins = 33%; cephalins = 22%; organic acids = 60.1%; glycerol = 8.1%; unsaponifiables = 22.7%; saponification value = 120–150; iodine number = 120; ash = 5.5–6.3%; nitrogen = 0.4%; phosphorus (P ₂ O ₅) = 4.8; sulfur is not present
E solids	0.3	Prolamines = 20%; sterolines = 80%; nitrogen = 1.9%; ash = 6.7%
F distillate (volatile components)	?	
G precipitate II	?	
H precipitate I	0.1	Nitrogen = 77%; ash = 25.0%; rubber = 20%; MgNH ₄ PO ₄ = 33%; raw proteins = 42%
Total solids (calculated)	42.4–43.6	
Common characteristics of the latex under investigation:		
Total solids	42.8	
Dry rubber content	39.7	Acetone extract = 2.20%; nitrogen = 0.48%; ash = 0.26%; copper = 0.10 mg. per 100 g. of rubber

Main fractions	Yield in percentage of latex	Characteristics (contents are expressed in percentage of the main fractions concerned)
Rubber hydrocarbon	37.6	Calculated from: $39.7 - \left(\frac{0.48}{100} \times 39.7 \times 6.25 + \frac{2.20 + 0.26}{100} \times 39.7 \right)$
Saponification value		120-150
Iodine value (Wijs)		120
Iodine value (Winkler)		114
Ash		5.5-6.3%
Nitrogen (Kjeldahl)		0.37%
Phosphorus as P_2O_5 (Liebig)		4.3%
Sulfur		not present

These figures, which were obtained according to methods described by Klein¹⁷, Jamieson¹⁸, Van Leent¹⁹ and others, give rise to the following remarks.

1. The difference between the iodine values found according to the methods of Wijs and Winkler should be attributed to the presence of a considerable quantity of sterols in the ether-soluble fraction of the latex. Indeed, McLean and Thomas²⁰ and Copping²¹ have shown that the Wijs method gives most abnormal values in the case of sterols, due to the substitution of notable quantities of halogens²².
2. The rather high ash content of the ether-solubles accounts for a complete analysis of the ash. The following approximate figures have been obtained²³: 83.7 per cent P_2O_5 ; 16.1 per cent MgO and 0.06 per cent CaO. From these data the conclusion can be drawn that the latex contains certain as yet, unidentified, magnesium compounds, which are soluble in ether. As a matter of fact, magnesium is a well-known carrier of phosphorus in plant physiology²⁴.
3. The nitrogen content mentioned above had to be controlled by a nitrogen estimation according to Dumas, since the nitrogen in choline, a derivative of lecithine, appears rather stubborn to Kjeldahlization²⁵.
4. According to Jamieson²⁶ the quantity of glycerol phosphatides can be approximately calculated by multiplying the percentage of P_2O_5 found by analysis by the factor 11.37. Hence the ether-soluble fraction contains $11.37 \times 4.83 = 54.92$ per cent glycerol phosphatides, this figure being in complete agreement with the percentage of 55, *i.e.*, the sum of the percentages of lecithins and cephalins found by the precipitation method described.

Conversely, the P_2O_5 content of 4.83 per cent found may be verified by the following considerations. One gram of the ether-soluble substances contains about 0.33 gram of lecithin and 0.22 gram of cephalins. Assuming these compounds to be present as oleostearo derivatives, in 0.33 gram of lecithins ($M = 805$) are present $0.33 \times \frac{71}{805} = 0.0291$ P_2O_5 , and in 0.22 gram of cephalins ($M = 745$): $0.22 \times \frac{71}{745} = 0.0210$ gram P_2O_5 . Thus from one gram of ether-solubles 0.0501 gram or 5.01 per cent P_2O_5 can be obtained. This figure is in good accordance with the percentage of 4.83.

FRACTION E: THE SOLIDS

The solids could be separated in an average yield of 0.33 per cent (the fraction contains 1.9 per cent nitrogen and 6.7 per cent ash). They appear to consist of about 20 per cent of proteinlike substances, probably prolamines,

ORGANIC ANALYSIS OF HEVEA LATEX

Fresh latex (1 part)
drop into 9 parts of 96% alcohol

Alcoholic solution
filter

Coagulated rubber
crepe thinly without washing
extract continuously in
Soxhlet apparatus the rubber crepe with: Filtrate
(add CaCO₃ powder)

Alcohol-extracted rubber
extract continuously with water

Alcoholic extract
filter

Extracted rubber
treat according to
Midgley, Henne and
Renoll¹⁸

Alcoholic extract
distill under reduced
pressure in CO₂
atmosphere

Aqueous residue
extract three times with
ether in a separatory funnel

Aqueous extract

Ethereal extract
evaporate to dryness

A
Rubber

B
Proteins

hydrolyze¹:
glycine
leucine
proline
arginine
lysine
histidine
aspartic acid
etc.

C
Water-solubles

analyze
organic components
quebrachitol
sugars
amines⁴
amides
amino acids²
etc.

D
Ether-solubles

glycerides, lecithins²,
cephalins, sterolesters, waxes, etc.
(saponify)
unsaponifiables:
sterols⁶
wax alcohols⁶
hydrocarbons
yellow coloring
matter (carotene)
etc.

E
Solids

prolamines
sugars
sterols
organic acids:
saturated fat
acids⁶
unsaturated
glycerol
fat acids⁶
resin acids⁶
hydroxy-,
dibasic acids
etc.

F
Distillate

recovered
alcohol of
±85%
volatile
compounds

W
Precipitate II

calcium carbonate
calcium phosphate
prolamines

F
Precipitate I

rubber particles
proteins
inorganic salts

besides about 80 per cent of complex sterolin substances²⁷. The first mentioned compounds are, in contrast to the latter, insoluble in boiling pyridine.

FRACTION F: THE DISTILLATE

The *distillate*, which is mainly composed of the recovered alcohol, most probably contains several volatile compounds of the latex. The investigation of these compounds obviously requires a special method of analysis to which the author intends to return in another communication.

FRACTION G: THE PRECIPITATE II

This fraction contains principally the excess of calcium carbonate added, besides calcium phosphate and coagulated prolamines. Its complete analysis is in progress.

FRACTION H: THE PRECIPITATE I

This *precipitate* (yield: 0.08–0.13 per cent), which contains 7.7 per cent nitrogen and 25 per cent ash, is separated roughly into its components by extracting the dry product continuously for several hours with benzene containing 5 per cent of absolute alcohol (soluble components about 20 per cent) and digesting the extraction residue with dilute hydrochloric acid (soluble components about 38 per cent). The residue, 42 per cent of the weight of the precipitate, contains chiefly proteins with an ash content of 2.2 percent and a nitrogen content of 12 per cent.

The fraction insoluble in benzene but soluble in dilute hydrochloric acid gives, on addition of ammonia, a relatively large quantity of magnesium ammonium phosphate, which is filtered out. The filtrate, on addition of sodium phosphate, gives an additional quantity of magnesium ammonium phosphate, showing that an excess of magnesium ions is present in the solution under investigation. The filtrate, moreover, appears to contain some calcium and copper salts.

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- ⁹ The data were obtained with the valuable assistance of Djûpri.
- ¹⁰ All yields recorded in this paper are expressed in percentages by weight, i.e., in grams per 100 grams of fresh unammoniated latex of clone Tjir I.
- ¹¹ The common characteristics of the crepe prepared in the usual way by acetic acid coagulation of the same latex are: acetone extract 2.20 per cent; nitrogen 0.48 per cent; ash 0.26 per cent, and copper 0.10 mg. per 100 grams of crepe. The latex itself had a total-solids content of 42.8 per cent and dry-rubber content of 39.7 per cent.
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INVERSE CORRELATION BETWEEN RUBBER HYDROCARBONS AND INSOLUBLES IN TOTAL SOLIDS OF LATEX FROM *HEVEA BRASILIENSIS* *

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Recent studies of the total solids in latex from the rubber-bearing plant *Cryptostegia grandiflora* indicated that a linear inverse correlation existed between the percentages of rubber hydrocarbons and a crystalline substance isolated from the insolubles¹. This stimulated a similar investigation into the relationship between rubber hydrocarbons and insolubles in the total solids of latex from *Hevea brasiliensis*.

Accordingly, thirty-four samples of latex from *Hevea brasiliensis* were collected and analyzed for rubber hydrocarbons and insolubles. In these samples a wide distribution of rubber hydrocarbons from low to high percentages was intentionally sought by bleeding petioles and stems of young seedlings as well as trunk-tapping mature trees in production. Except for six collections, the latex was air-dried on a glass sheet immediately on exudation. When it was dry enough to allow handling, it was removed from the sheet and further dried to constant weight at 60° C. The dried latex, called "latex total solids", formed the basis on which percentage composition was calculated. The six latex samples not dried on a sheet of glass immediately after exudation were "rubber biscuits" formed in commercial latex collecting cups as remnants of dried latex from the previous tapping. All latex samples were collected from April, 1944, to March, 1945, from two widely separated locations in Mexico and from two locations in Costa Rica. Because of the low yields of latex from petioles and seedlings, these samples were composite collections from five to forty individuals. The trunk latex samples from producing trees of seedling origin were analyzed on an individual tree basis. This allowed for more variation between samples than if they had been composited. The considerable diversity represented by the collections is shown (Table I).

Duplicate analyses of the total solids for rubber hydrocarbons were made by a bromination technique, while insolubles were determined gravimetrically¹. By these methods, both rubber hydrocarbons and insolubles were determined directly. This is an important point since these two fractions together constitute a large percentage of the total solids. If, therefore, either of them was determined indirectly by difference, an apparent correlation could be indicated, though actually nonexistent. According to these analytical methods, insolubles in total solids are defined as substances which are insoluble in either acetone or benzene; rubber hydrocarbons are benzene-soluble substances which form bromides insoluble in 95% ethyl alcohol.

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TABLE I
ANALYSES OF LATEX SOLIDS FROM *Hevea brasiliensis*. UNLESS INDICATED OTHERWISE, LATEX WAS COLLECTED BY TRUNK TAPPING.
TRUNK LATEX SAMPLES ARE FROM INDIVIDUAL TREES; ALL OTHER SAMPLES ARE COMPOSITE YIELDS OF FROM 5 TO 40 INDIVIDUALS

Date	Latex source and tree age	Location	Latex analyses		
			Rubber hydrocarbon %	Insolubles %	Undetermined (difference) %
Mar. '45	Leaf petioles	El Palmar, V. C., Mexico	47.3	36.7	16.0
Mar. '45	1-4 inch diam. green lat. br.	El Palmar, V. C., Mexico	49.3	39.4	11.3
May '44	Mature petioles, 14-yr. seedling	Gomez Farias, Tps., Mexico	49.4	34.3	16.3
Mar. '45	1-4 in. gr. side branches	El Palmar, V. C., Mexico	52.3	34.0	13.7
Mar. '45	Leaf petioles on 2-yr. tree	El Palmar, V. C., Mexico	54.0	33.0	13.0
July '44	Stems, seedlings	Turrialba, Costa Rica	54.6	33.0	12.4
Aug. '44	Mature petioles on 10-mo. seedling	El Palmar, V. C., Mexico	65.9	22.1	12.0
July '44	Petiole young leaf, clone GV-21	El Palmar, V. C., Mexico	67.3	21.3	11.4
Apr. '44	Stems, 15-month seedlings	El Palmar, V. C., Mexico	68.6	17.4	14.0
July '44	Mature petioles, 3-yr. seedling	El Palmar, V. C., Mexico	69.7	19.0	11.3
July '44	Petiole young leaf, clone GA-49	El Palmar, V. C., Mexico	70.5	18.7	10.8
Mar. '45	Two years, group B	El Palmar, V. C., Mexico	70.7	18.0	11.3
Mar. '45	Two years, group A	El Palmar, V. C., Mexico	71.5	13.3	15.2
May '44	Estimated 2 years	Gomez Farias, Tps., Mexico	72.0	10.0	18.0
May '44	Estimated 1 1/2 years	Gomez Farias, Tps., Mexico	73.3	10.6	16.1
July '44	Clone GA 49, stem 1 inch diam.	El Palmar, V. C., Mexico	73.7	16.7	9.6
Mar. '45	Two years, group A	El Palmar, V. C., Mexico	75.2	13.3	11.5
Mar. '45	Two years, group B	El Palmar, V. C., Mexico	75.6	20.3	4.1
July '44	Clone GV-21, stem 1 inch diam.	El Palmar, V. C., Mexico	76.9	12.9	10.2
Apr. '44	In production, estimated 20 yrs.	El Palmar, V. C., Mexico	77.7	4.7	17.6
July '44	Plantation A, 3 years	El Palmar, V. C., Mexico	77.8	9.8	12.4
July '44	Seedling, 1 1/2 years	El Palmar, V. C., Mexico	78.3	9.8	11.9
July '44	Plantation B, 3 years	El Palmar, V. C., Mexico	78.4	10.8	10.8
July '44	In production, seedling origin	Cairo, Costa Rica	81.5	1.4	17.1
July '44	In production, seedling origin	Cairo, Costa Rica	82.0	1.7	16.3
July '44	In production, seedling origin	Cairo, Costa Rica	82.2	2.2	15.6
July '44	In production, seedling origin	Cairo, Costa Rica	82.8	4.0	13.2
July '44	In production, seedling origin	El Palmar, V. C., Mexico	83.0	3.3	13.7
July '44	In production, seedling origin	El Palmar, V. C., Mexico	83.2	5.4	11.4
July '44	In production, seedling origin	El Palmar, V. C., Mexico	84.2	2.8	13.0
July '44	In production, seedling origin	Cairo, Costa Rica	84.3	0.6	15.1
July '44	In production, seedling origin	Cairo, Costa Rica	84.9	1.6	13.5
July '44	In production, seedling origin	Cairo, Costa Rica	85.7	0.4	13.9
July '44	In production, seedling origin	Cairo, Costa Rica	89.0	1.1	9.9

From these analyses, it was found that the percentage of rubber hydrocarbons was inversely correlated with the insolubles (Table I and Figure 1). The correlation coefficient between percentage of rubber hydrocarbons and insolubles was -0.970 . Since these analyses appear to represent a straight line relationship, it was possible, by using the method of least squares for the computation of regression averages, to calculate the equation:

$$R\% = 86.6 - 0.972 I\%$$

where R = rubber hydrocarbons and I = insolubles. The line defined by this equation (Figure 1) has intercepts of 86.6 and 89.2 on the rubber hydrocarbons

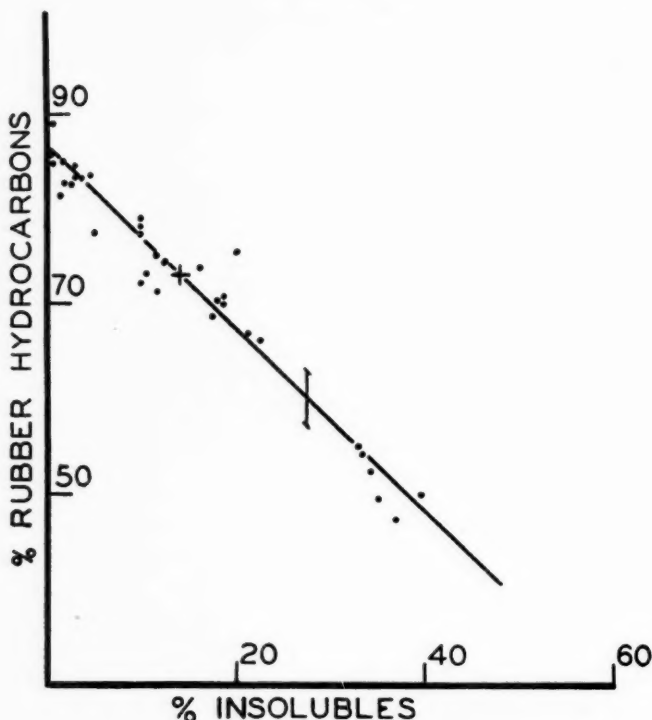


Fig. 1.—Inverse correlation between percentage of rubber hydrocarbons and insolubles in total solids of latex from *Hevea brasiliensis*. Regression line with standard error calculated from 34 analyses. Cross shows average point.

and insolubles axes, respectively. The standard error of the estimate was ± 2.8 per cent. The regression coefficient, -0.972 , is significant at the 1 per cent level. The corresponding regression coefficient for a similar relationship in latex from *Cryptostegia grandiflora* was -0.809 .

The significance of the inverse correlation between rubber hydrocarbons and insolubles in latex from *Hevea brasiliensis* is not yet understood. Isolation and identification of the substance, or substances, in the insolubles which cause the correlation may indicate if this relationship is caused by the presence of rubber hydrocarbon "precursor" in the insolubles or by some other means.

It is clear that the correlation affords a basis for further physiological studies on latex rubber formation. The fact that a similar relationship exists in the latex from rubber-producing plants of two different botanical families may indicate that it is of a fundamental nature.

ACKNOWLEDGMENT

The authors thank F. J. LeBeau and T. J. Grant for their help in making the latex collections in Mexico and Costa Rica.

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**FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY**

CHICAGO, ILLINOIS

SEPTEMBER 10-13, 1946

The 110th Meeting of the American Chemical Society was held in Chicago, September 9-13, 1946. The meetings of the Division of Rubber Chemistry, including the High Polymer Forum, extended from Tuesday, September 10 through Friday, September 13. The headquarters of the Division were at the Sherman Hotel, where the technical sessions, banquet, and committee meetings were held. The local arrangements were handled by a committee of the Chicago Rubber Group, under the chairmanship of Francis S. Frost, Jr., with

Bruce Hubbard, Chairman of Housing; H. A. Winklemann, Chairman of Banquet and Entertainment; William Crumpler, Chairman of Registration and Ticket. The attendance of members of the Division was estimated at 800 out of a total registration for the whole Society of somewhat over 9,000.

The combined programs of the Division and of the Polymer Forum comprised 58 papers. The general topic of synthetic rubber again received major attention, with 44 authors devoting themselves to the various phases of polymer chemistry, *e.g.*, the fundamentals of polymerization and the synthesis of numerous polymeric systems, and the properties, manufacture and compounding of the synthetic elastomers now commercially available. In opening the technical sessions, Chairman Gibbons commented on the steady growth of the Division and its increased opportunities to serve its members and the rubber industry in general. He pointed out the value of closer and more active collaboration between the Local Rubber Groups and the Division, if this opportunity is to be realized to the fullest.

The following papers were presented in five half-day sessions:

1. W. A. GIBBONS. Introduction.
2. JOHN T. HAYS, ARTHUR E. DRAKE, AND YOLANDA T. PRATT. Disproportionated Rosin Soap (Dresinate-731) as Emulsifier in GR-S Polymerization.
3. CHARLES F. FRYLING. Emulsion Polymerization of Synthetic Rubber with Dehydrogenated Rosin Soap and Tertiary Mercaptan Modification.
4. A. J. JOHANSON AND L. A. GOLDBLATT. Emulsion Copolymerization of Isoprene and Styrene.
5. A. M. BORDERS AND R. M. PIERSON. Relation of Latex Droplet Size to Synthetic-Rubber Properties and High-Solids Latex Fluidity.
6. FREDERICK W. BREUER. The Effect of Traces of Inhibitors on Synthetic-Rubber Polymerizations.
7. J. C. MADIGAN, E. L. BORG, R. L. PROVOST AND W. J. MUELLER. Development of GR-S 65, a Low Water-Absorption Polymer for Electrical Insulation.
8. W. R. HUCKS. Governmental Activities in the Production of Synthetic Rubber.
9. ALFRED SAFFER AND B. L. JOHNSON. The Measurement of Internal Double Bonds in Polymers by Perbenzoic Acid Addition.
10. J. D. D'IANNI. Effects of Side Vinyl Groups and Other Structural Features on Physical Properties of Diene Polymers.
11. G. E. SERNIUK, F. W. BANES AND M. W. SWANEY. A Study of Reaction of Buna Rubbers with Aliphatic Mercaptans.
12. IRA WILLIAMS. Charles Goodyear Medal address. The Vulcanization of Rubber with Sulfur.
13. ROBERT D. STIEHLER AND JAMES H. WAKELIN. Studies on Vulcanization: Mechanism and Theory.
14. B. M. STURGIS, A. A. BAUM AND J. H. TREPAGNIER. Vulcanization of GR-S with Halogen Compounds.
15. NORMAN RABJOHN AND PAUL J. FLORY. The Synthesis of Esters of Azodicarboxylic Acid and Their Reactions with Rubber.
16. R. L. ZAPP. Polymeric Unsaturation and the Relative Rate of Cross-Linkage.
17. A. L. BLACK. Relationship between Gel Content, Plasticity, and Dilute Solution Viscosity of Elastomers.

18. J. REID SHELTON AND HUGH WINN. Comparison of the Effects of Oven and Bomb Aging at Corresponding Temperatures.
19. J. H. FIELDING. Exposure Cracking of Rubber.
20. L. R. SPERBERG, L. A. BLISS AND J. F. SVETLIK. Compression Set as a Relative Measure of State of Cure.
21. FRITZ S. ROSTLER AND HUBERT I. DU PONT. Plasticizer-Filler Mixtures and Their Dispersion in Rubber.
22. L. O. AMBERG. GR-S-10 Compared with GR-S in Vulcanizates Containing Various Fillers.
23. HARRY L. FISHER AND ARNOLD R. DAVIS. An Improved Method of Compounding Pure-Gum GR-S Stocks.
24. J. J. KEILEN AND A. POLLAK. Lignin for Reinforcing Rubber.
25. J. L. STIEF AND J. J. BOYLE. Effect of Fungicides on Rubber.
26. H. E. ALBERT AND G. W. GOTTSCHALK. The Effect of Iron on the Aging of GR-S.
27. L. S. VERDE, R. H. DUDLEY AND L. B. TURNER. Butyl Inner Tubes. Growth in Service.
28. P. C. SERVAIS. The Composition and Properties of Silastic.
29. H. H. GILLMAN AND RAY THOMAN. Behavior of Rayon Tire Cord during Latex Dipping.
30. E. B. NEWTON, W. D. STEWART AND E. A. WILLSON. Crude Rubber Preparation. Sheet Production by Continuous Coagulation of Hevea Latex.
31. D. E. WOODFORD, C. S. WILKINSON, JR. AND S. D. GEHMAN. Low-Temperature Characteristics of Elastomers.
32. C. M. DOEDE AND A. PFENNINGER, JR. The Effect of Gaseous Environment on the Dielectric Strength of Synthetic and Natural Rubber Compounds.
33. GEORGE D. SANDS AND B. L. JOHNSON. Description of a Complete Osmotic Molecular-Weight Apparatus.

The High Polymer Forum was sponsored by the Division of Physical and Inorganic Chemistry, with the Divisions of Cellulose, Colloid, Organic and Rubber Chemistry collaborating. The chairmanship of the sessions of the Forum was divided between H. Mark, H. I. Cramer and H. M. Spurlin. The Polymer program follows:

1. H. MARK. Introduction.
2. HOMER JACOBSON AND W. H. STOCKMAYER. Intramolecular Reaction in Polycondensations. I. The Theory of Linear Systems.
3. WERNER KUHN. Double Refraction in Systems Containing Kinked Chain Molecules.
4. GUY B. TAYLOR. The Distribution of the Molecular Weight of Nylon as Determined by Fractionation in a Phenol-Water System.
5. W. E. DAVIS. The Effect of Molecular-Weight Distribution on the Viscosity-Concentration Coefficient.
6. R. H. WAGNER. The Application of Corrections in the Viscometry of High Polymer Solutions.
7. W. D. HARKINS. Further Relations Concerning the Mechanism of Emulsion Polymerization.
8. L. M. WELCH, M. W. SWANEY, R. F. HOWE, A. H. GLEASON AND R. K. BECKWITH. Initiation and Growth of Butadiene Resinous Polymers.

9. G. E. SERNIUK, F. W. BANES AND M. W. SWANEY. A Study of Reaction of Buna Rubbers with Aliphatic Mercaptans.
10. WENDELL V. SMITH. Regulator Theory in Emulsion Polymerization.
11. A. J. JOHANSON AND L. A. GOLDBLATT. Emulsion Copolymerization of Isoprene and Styrene.
12. DEBORAH MORGAN, R. L. GUILLE AND R. C. HUSTON. Emulsion Polymerization of Styrene.
13. CHARLES H. HOFRICHTER, JR. AND A. DOUGLAS McLAREN. The Temperature Dependence of the Adhesion of High Polymers to Cellulose.
14. J. F. SAEMAN, E. E. HARRIS AND A. A. KLINE. The Kinetics of the Hydrolysis of Cellulose.
15. M. T. O'SHAUGHNESSY, JR. The Creep of Viscose Rayon.
16. SHERMAN E. SMITH. The Sorption of Water Vapor of High Polymers.
17. P. E. ROUSE, JR. Diffusion of Vapors in Films.
18. PAUL M. HAUSER AND A. DOUGLAS McLAREN. Permeation through and Sorption of Water Vapor of High Polymers.
19. W. M. D. BRYANT. Polythene Fine Structure.
20. DONALD F. WILCOCK. Liquid Methylpolysiloxanes.
21. R. BUCHDAHL, R. BRADDICKS, JR. AND P. V. MCKINNEY. Pigment Dispersions. Intrinsic Viscosity and Dimensions of Colloidal Carbon in Water.
22. PAUL O. POWERS. Solubility of Low Polymers of Styrene.
23. DONALD E. ROBERTS, WILLIAM W. WALTON AND RALPH S. JESSUP. Heats of Combustion and Solution of Liquid Styrene and Solid Polystyrene and the Heat of Polymerization of Styrene.
24. SAUL G. COHEN. Inhibition and Retardation of the Peroxide Initiated Polymerization of Styrene.
25. WILFRIED HELLER AND H. B. KLEVENS. Spectrophotometric-Interferometric Particle Size Determinations in Synthetic Latices and Bearing of the Results on the Theory of Emulsion Polymerization.

The Charles Goodyear Medal Address was presented by IRA WILLIAMS, the fourth recipient of this award. His subject was "The Vulcanization of Rubber with Sulfur".

In the business meeting Thursday afternoon, September 12, C. A. Bartle, Head Teller, reported the election, by the letter-ballot sent out in August, of the following officers for 1946-1947:

Chairman	—W. W. Vogt
Vice-Chairman	—H. E. Outcault
Secretary	—C. R. Haynes
Treasurer	—C. W. Christensen
Sergeant-at-Arms	—L. M. Baker
Directors:	—W. A. Gibbons
	R. A. Schatzel
	G. L. Allison
	A. M. Neal
	G. H. Swart
	C. C. Davis
	S. G. Byam

The letter-ballot was unanimously ratified by a vote of the members in attendance at the meeting.

The chairman of the Membership Committee, H. E. Outcault, reported a continuing growth of the Division, the present membership being 1351 Active and 267 Associate members, or a total of 1618.

Dr. Gibbons, as the retiring Chairman, expressed his appreciation of the fine coöperation and support accorded him during his term of office by the members, the Directors and the other officers of the Division. He presented W. W. Vogt, Chairman-elect, who outlined briefly plans of the Division for the coming year.

The joint luncheon of the Officers of the Local Rubber Groups and of the Division was held on Friday noon, September 13. At this luncheon plans were laid whereby better scheduling of speakers appearing before the various Groups could be realized. In view of the importance of the problems involved in the processing and handling of synthetic and natural rubbers in the postwar period, it was agreed that all the program committees of all Groups should include this topic in their papers program for the coming year.

The Divisional Banquet, held Thursday evening, will long be remembered by those attending as one of the finest in the history of the Rubber Division. The Division is indeed indebted to Mr. Frost and his committee for having arranged such an outstanding program of entertainment. The attendance at this function was approximately 1000. Among the guests were Alden H. Emery, Secretary of the American Chemical Society, and Walter H. Murphy, Editor of *Industrial and Engineering Chemistry*.

H. I. CRAMER
Retiring Secretary

NEW BOOKS AND OTHER PUBLICATIONS

1940-41 BIBLIOGRAPHY OF RUBBER LITERATURE (Including Patents). Published by the Division of Rubber Chemistry of the American Chemical Society. Sold by *The Rubber Age*, 250 W. 57th St., New York 19, N. Y. Cloth, 6 by 9 inches, 296 pages. Price \$5.—This bibliography, the fifth in this series on rubber literature and the first edition under the sponsorship of the Division of Rubber Chemistry, was compiled, edited, and prepared by the Division's bibliography committee, consisting of C. C. Davis, M. E. Lerner, C. W. Christensen, and John McGavack, Chairman. The previous editions were compiled by D. E. Cable and published by *The Rubber Age*.

The current edition continues the letter-number combination method of identifying references, which expedites the use of cross-references and indices. For the first time patent references are included, and brief one-sentence abstracts are given with each reference. The new volume shows a consequent increase in the number of pages devoted to references, with 172, compared with 16 pages in the 1938-39 edition. Some changes have been made in the classification groups, some being merged and others being subdivided, to agree with further developments in rubber technology. As in previous editions, comprehensive author and subject indices appear.

No critical review of this bibliography is necessary; the reception accorded to previous editions has amply demonstrated the value of these volumes in directing literature searches on published work in the rubber field. [From the *India Rubber World*.]

LE CAOUTCHOUC D'HEVEA: INITIATION AUX METHODES D'EXPLOITATION EN INDOCHINE. (HEVEA RUBBER: INTRODUCTION TO METHODS OF CULTIVATION IN INDO-CHINA). Published by Institut Français du Caoutchouc, 42 Rue Scheffer, Paris, France. $7\frac{1}{2} \times 11$ in. 160 pp.—400 francs (approximately \$4.00). (In French).—This book has a two-fold purpose, first to outline methods of rubber cultivation as practiced in Indo-China and, second, to encourage young planters, botanists and agriculturists to investigate and embrace the rubber cultivation field. It is divided into three parts, the first devoted to a brief history of the rubber industry, descriptions of *Hevea brasiliensis* and other rubber-yielding plants, and the functions, collection and composition of latex; the second, more pertinent to cultivation, covers suitable climatic and soil conditions, selection and reproduction of high-yielding trees, density of planting, diseases of rubber trees, harvesting of latex, coagulation, sheeting, preparation of crepe, and preparation of specialty rubbers, such as powdered rubber; the third briefly describes the properties of raw and vulcanized rubber and some of the basic methods used in the manufacture of end products. The book is profusely illustrated with excellent photographs depicting every phase of rubber cultivation. [From *The Rubber Age* of New York.]

EMULSION TECHNOLOGY: THEORETICAL AND APPLIED. (SECOND EDITION). Edited by H. Bennett. Published by the Chemical Publishing Co., Inc., 234 King St., Brooklyn 31, N. Y. $5\frac{1}{2} \times 8\frac{1}{2}$ in. 360 pp. \$6.50.—“Enlarged, and containing a comprehensive section on the theory of emulsion and emulsifying agents, this second edition of “Emulsion Technology” has been completely revised and brought up to date. Handled in the form of a symposium, with sections contributed by leading authorities, the book covers the application of emulsions in many industries and technical processes. A special feature of the new edition is a comprehensive list of emulsifying agents divided into the following categories: Anion Active Agents, Cation Active Agents, Nonionic Agents, and Miscellaneous Emulsifiers. This list, arranged alphabetically, includes trade names, chemical composition, emulsion type, references, manufacturer, and recommended uses of the emulsifying agents. A 13-page chapter on “Rubber Latex” was contributed by H. P. Stevens and W. H. Stevens, consultants to the Rubber Growers' Association. A subject index is included. [From *The Rubber Age* of New York.]

MODERN ORGANIC FINISHES. By Rollin H. Wampler. Published by the Chemical Publishing Co., Inc., 234 King St., Brooklyn 31, N. Y. $5\frac{1}{2} \times 8\frac{1}{2}$ in. 452 pp. \$8.50.—Prepared for industrial users of organic protective and decorative coatings, this book is primarily one of methods. Descriptions of modern finishing materials and of equipment for application, drying, and conveying are presented so that the reader may have an overall picture of modern industrial finishing operations. Throughout the text, the main emphasis is on proper selection and proper use of materials and equipment to get the best possible finish at minimum cost. The book is divided into six sections, as follows: Modern Organic Finishing Materials; Modern Application Methods; Drying Methods; Product Handling in the Finishing Department; Finishing Processes; General Considerations. Brief reference is made in the book to rubber-base paints. A special bibliography and a subject index are included. [From *The Rubber Age* of New York.]

HANDBOOK OF CHEMISTRY. (6TH EDITION). Compiled and Edited by Norbert Adolph Lange. Published by Handbook Publishers, Inc., Sandusky, Ohio. $5\frac{3}{8} \times 7\frac{3}{4}$ in. 2082 pp. \$7.00.—The latest edition of this veritable one-volume library of chemical and physical data has been carefully revised and brought up to date. As the compiler indicates in his preface, perhaps the most important change in the edition is the completely revised and enlarged table of Physical Constants of Inorganic Compounds. This table has been increased to include over 2600 compounds, with a corresponding list of more than 1300 synonyms. For the first time, wherever possible, data on refractive index have been included in the table. Considerable subject matter not in the previous edition is now incorporated, including modern concepts of matter, and numerical values of the gas constant. Eleven tables, including that mentioned above, have been extended or completely rewritten, and two tables and some data on the strictly engineering aspects have been dropped. As in past editions, the extensive index, which covers more than 3600 entries, is unusually complete. [From *The Rubber Age* of New York.]

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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SECOND FOUNDATION LECTURE

of the Institution of the Rubber Industry

"THE IMPACT OF SYNTHESIS ON THE RUBBER INDUSTRY"

By

PHILIP SCHIDROWITZ

(Colwyn Medallist for 1940)

in the Grand Hall of the Connaught Rooms,
Great Queen Street, London, W. C.,
Friday, June 6, 1947, at 5.30 P.M.

To be Followed by a Dinner at 7.30 P.M.

The "Foundation Lecture" was established by the Council of the I.R.I., and is now an important occasion in the annual functions of the Institution. The choice of lecturer is confined to authorities of international standing, and Dr. Schidrowitz has a world-wide reputation.

About two years ago, soon after the celebration of the 25th anniversary of the well-known feature in the *India-Rubber Journal*, "Views and Reviews," contributed by Dr. Schidrowitz, many of the industry's foremost personalities gathered to pay tribute to this versatile and accomplished chemist.

Invitations have been extended to distinguished members of the State, of science and of industry, to dignify the assembly which will honor Philip Schidrowitz, on June 6. It is hoped that as many friends as possible will come from overseas to add still further lustre to this great occasion.

The lecturer will not confine his address to synthetic rubbers, but will also discuss plastics and other relevant materials. The broad question of natural rubber *versus*, or in relation to, man-made materials will receive consideration. Reference will be made to the possibility of fusion or closer relationship between the rubber and plastics industries.

Admission will be by ticket, and early application is requested to the Secretary, I.R.I., 12, Whitehall, London, S.W. 1.

A limited amount of hotel accommodation has been reserved, and every effort will be made to meet personal needs. Should such accommodation for overseas visitors prove inadequate, members of the London Section of the I.R.I. will doubtless offer the hospitality of their homes.

NEW BOOKS AND OTHER PUBLICATIONS

FIVE YEARS OF SYNTHETIC RUBBER. United States Rubber Co., Rockefeller Center, New York 20, N. Y. 50 pages.—Intended for students, educators, and interested members of the public, this booklet in simple language shows the growth of the synthetic rubber industry and gives an appraisal of its present-day importance in the manufacture of rubber products. Section headings cover synthetic rubber before the War; the types of synthetic rubber; the discovery of synthetic rubber; the Government rubber program; present status of the synthetic rubbers; manufacture of GR-S; uses of natural and synthetic rubber in tires; reconversion to natural rubber; and what materials are polymers. There are also three technical appendices covering comparative properties of natural and synthetic rubber, chemical structure of rubber, and a glossary of technical terms. [From the *India Rubber World*.]

NOTRE CAOUTCHOUC D'INDOCHINE (OUR INDO-CHINA RUBBER). Issued by Institut Français du Caoutchouc, 42 Rue Scheffer, Paris, France. $8\frac{1}{4} \times 10\frac{1}{4}$ in. 36 pp. (In French).—Published under the auspices of La Fédération Nationale des Producteurs de Caoutchouc, Gommés et Résines, in coöperation with L'Institut Français du Caoutchouc, this booklet, as indicated by its title, covers the cultivation of rubber in Indo-China. It discusses the location of rubber plantations in the country, the early trials and tribulations of rubber cultivation, and some of the lessons learned as a result of actual accomplishment. The effect of the war on the rubber industry in Indo-China is also discussed, as well as the future potential of the country. In the latter regard, considerable space is devoted to a discussion of the applications of rubber in various fields, including home and industry. [From *The Rubber Age of New York*.]

BUTALASTIC POLYMERS. THEIR PREPARATION AND APPLICATIONS. A TREATISE ON SYNTHETIC RUBBERS. Frederick Marchionna. vii + 642 pages. Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y., 1946. Price, \$8.50.—Marchionna has taken advantage of his long experience as examiner in the United States Patent Office to compile this very extensive summary of published information on synthetic rubbers. As would be expected, it emphasizes most strongly the patent literature, listing over 600 United States patents. Marchionna himself, after warning the reader that "a good part of the patent literature may be in some part misleading or make claims for prod-

ucts which have never been produced," attempts to summarize all the patents as completely as practicable. One finds summaries of the periodical literature extending back into the earlier eras of synthetic rubber, with discussion of the work of such pioneers as Tilden, Harries, Hoffmann, Ipatieff, Kondakov, Lebedev, and Ostromislensky.

With such complete coverage of the older material it is unfortunate that wartime delays in printing the book apparently made it impossible for Marchionna to mention any patents or periodical literature published later than 1943. This delay presumably explains the fact that the wartime synthetic rubber program of the United States is not given the attention it deserves in a book published in 1946. For example, one searches in vain for mention of GR-S, GR-I, or GR-M, and notes that the latest statistics on the output of synthetic rubber in the United States are the anticipated production for 1943. The word *butalastic* is introduced by Marchionna to describe the elastic or plastic polymers of butadiene and its derivatives, polymerized alone or with other compounds. He divides the butalastics into 17 different classes, depending on the chemical nature of the monomers. Part I is devoted to the source and production of the monomers; Part II, comprising about half the book, to the mechanism and processes of polymerization; and Part III, to the processing, properties, and applications of the butalastics. The author uses the term *interpolymer* for polymers containing different monomeric units in the same chain and *copolymer* for a mixture of different polymers.

The book brings together in one volume a great amount of detailed information not otherwise readily accessible. For example, about 500 catalysts of polymerization are listed. There is a 30-page general index. [LAWRENCE A. WOOD in *Chemical & Engineering News*.]

THE RUBBER INDUSTRY. (REVISED). By Josephine Perry. Published by Longmans, Green & Co., Inc., 55 Fifth Ave., New York 3, N. Y. 6 × 8 in.-128 pp. \$2.00.—The present volume of this work, published as part of the "America at Work" series, is a new, enlarged and completely revised edition of the author's earlier volume on the rubber industry (1941). Like the first edition, it is a brief account of the growth and development of the sprawling rubber industry, but this time adds the story of the American development of synthetic rubber to meet the country's need for an indispensable raw material. The importance of rubber research is stressed in the present volume. Intended for students and others wishing to familiarize themselves with the rubber field, it contains brief data on the manufacture of various rubber products, including tires, footwear, mechanical goods, and latex applications. [From *The Rubber Age* of New York.]

ELASTOMERIC ENGINEERING. Published by Andre Rubber Co., Ltd., Kingston By-Pass, Surbiton, Surrey, England. 7½ × 10 in. 168 pp. Price: One Guinea (approximately \$4.50).—Prepared for the practical use of engineers, this book is a useful guide in the manufacture and application of rubber-to-metal units of all kinds. In addition, it serves to give the reader some background on rubber itself, the first few chapters being devoted to preparation of raw natural rubber, manufacture of synthetic rubber, compounding and processing of natural and synthetic rubbers, and properties of these rubbers. The greater portion of the book is concerned with rubber-to-metal bonding, including chapters covering the following specific subjects: bonding rubber to metal;

properties of the rubber-metal bond; testing and design of bonded units design of molding equipment; design formulas and calculations for bonded rubber units; and rubber in chemical engineering. Some information on Andre products and their applications in industry, as well as data on the company's research and development facilities, is included. One chapter is devoted to an explanation of some of the terminology employed in the rubber field. [From *The Rubber Age* of New York.]

RAPID PHOTOMETRIC METHOD FOR DETERMINING RUBBER AND RESINS IN GUAYULE TISSUE AND RUBBER IN CRUDE RUBBER PRODUCTS. Hamilton P. Traub, United States Department of Agriculture, Washington, D. C. Technical Bulletin No. 920, August, 1946. 37 pages.—This technical report describes rapid semimicrophotometric methods for determining rubber and resin in small samples of guayule tissue. These methods are also adaptable to other rubber and resin bearing plants, to the determination of rubber in crude rubber products, and to the analysis of synthetic rubbers. Procedures and experimental results are given, together with a summary and a list of literature cited. [From the *India Rubber World*.]

DIFFERENTIATION OF RUBBER AND GUTTA HYDROCARBONS IN PLANT MATERIALS. By S. B. Hendricks, S. G. Wildman, and E. J. Jones. Issued by the Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Md. 6 × 9 in. 12 pp.—Reprinted from the *Archives of Biochemistry*, this report covers the work undertaken to determine whether certain polymerized hydrocarbons isolated from various plants can be designated as being either rubber or gutta, and to provide an initial approach to the biochemical problem as to the manner in which such polymers are made by plants. Since chemical reactions were found to be of little value in identifying the isomers because the same end products were obtained when the double bonds of the molecules were destroyed, the investigators employed a nonrecording spectrograph for infrared transmission measurements. The results indicate that the hydrocarbons of rubber and gutta isolated from a variety of plants, including *Hevea brasiliensis*, *Mimusops balata*, and *Asclepias erosa*, can be positively identified by their light absorptions near 12 μ . Mixed *cis*- and *trans*-isomers were absent in all cases even though the plants examined were selected as giving hydrocarbon polymers of questionable types. [From *The Rubber Age* of New York.]

EMULSION TECHNOLOGY. Theoretical and Applied. Including the Symposium of Technical Aspects of Emulsions. Second Edition. Chemical Publishing Co., Inc., 26 Court St., Brooklyn 2, N. Y. Cloth, 8½ by 5½ inches, 368 pages. Index. Price \$6.50.—This volume like the original edition, contains the contributions of twenty European colloid scientists and consists, with some revisions and additions, of the papers presented at the second symposium on emulsions sponsored by the British Section of the International Society of Leather Trades Chemists. These sections are essentially unchanged from the first edition, but the new book also contains a comprehensive section on the theory of emulsions and emulsifying agents by G. M. Sutheim, an American specialist. Included in this section is an up-to-date list of emulsifying agents classified in the following groups: anion-active, cation-active, nonionic, and

miscellaneous. It lists in addition to the commercial and/or chemical name, the chemical composition, the type of emulsion it helps to produce, physical properties, suggested uses, and manufacturers of the emulsifying agents.

The initial chapters deal with the mechanics and fundamental principles of emulsification. Following are sections dealing with the use of emulsions in medicine, agriculture, and industry. Chapters on the design of emulsifying machinery, industrial formulations, and emulsion properties are also included, besides a chapter on emulsions in the patent literature containing some 244 references. Concluding the volume is the new chapter on theory of emulsions and the list of emulsifying agents. Each chapter contains many literature references. [From the *India Rubber World*.]

SOAP IN INDUSTRY. Georgia Leffingwell and Milton Lesser. Chemical Publishing Co., Inc., 26 Court St., Brooklyn 2, N. Y. Cloth, $8\frac{3}{4}$ by $5\frac{1}{2}$ inches, 210 pages. Price, \$4.—As stated in the introduction, this book is intended to be an indicative rather than an exhaustive survey of the industrial uses of soluble soaps (potash and soda soaps as contrasted with the heavy metal soaps), with particular emphasis on the growing place of these soap uses in our industry.

Each chapter is devoted to a particular industry and discusses the use of soaps in that industry. Formulations and results obtained are given together with comprehensive literature references. Industries thus discussed include animal husbandry, building and construction, cosmetics, dentistry, inks and ink making, insecticides, leather, lubricants, milk production, mining and ore treating, oil production, paints, paper and packaging, plastics, metal, glass and wood polishes and cleaners, restaurant sanitation, road building and maintenance, rubber production, textiles, dyeing and printing textiles, wool production.

The chapter on rubber production gives brief discussions of the use of soap in emulsion polymerization of synthetic rubbers, preparation of reclaimed rubber dispersions, emulsification of latex compounding ingredients, stabilization of emulsions, mold lubricants and dusting agents, stabilization of foam sponge rubber, preparation of rubber adhesives, and as an ingredient in latex purification. The chapter on plastics similarly covers the use of soaps in emulsion polymerization of resins, and the many types of resin emulsions. [From *The India Rubber World*.]

CHEMICAL ENGINEERING CATALOG, 1946-47. Thirty-First Annual Edition. Reinhold Publishing Corp., 330 W. 42nd St., New York 18, N. Y. Cloth, 11 by 8 inches, 1768 pages. Price: free to domestic members of industry; \$7.50 to foreign subscribers.—The current edition of this standard reference volume continues to give data on equipment, supplies, chemicals, and materials in the chemical industry, as provided by more than 600 companies. Representing an increase in size of 60 pages over the previous 1945-46 edition, the book contains enlarged sections on suppliers of equipment and chemicals. As in previous editions, a valuable index of trade names is also included. The section on technical and scientific books has again been curtailed, and it lists only those books in print by the publisher and by the publishers cooperating in this section of the Catalog. [From the *India Rubber World*.]

INDUSTRIAL RESEARCH LABORATORIES OF THE UNITED STATES. Compiled by Callie Hull. Published by the National Research Council, National Academy of Sciences, Washington, D. C. $6\frac{3}{4} \times 9\frac{3}{4}$ in. 415 pp. This is the eighth edition of this directory which furnishes valuable information on the industrial research laboratories of the United States, including consulting research laboratories. An appendix has been included for the first time in the present edition, listing colleges and universities which offer research service to industry. The data included are fresh and up-to-date, as no unrevised material is included. The laboratories are listed in alphabetical order, with information furnished on personnel and services rendered. Three special indexes are included, *i.e.*, a geographical distribution of laboratories, a personnel index, and a subject index of research activities. [From *The Rubber Age* of New York.]

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Dayton, Ohio

NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1945. Published by W. Heffer & Sons, Ltd., Cambridge, England, for the Institution of the Rubber Industry, 12 Whitehall, London, S. W. 1, England. $7\frac{1}{4} \times 9\frac{3}{4}$ in. 120 pp. Price: To members, 4/6 (approximately \$1.25); to nonmembers, 12/6 (approximately \$3.25).—The latest of these annual reports, compiled by the Institution of the Rubber Industry, is the ninth to be published. Again each branch of the overall rubber field is covered by a well qualified expert, with bibliographical references to journals and patents at the end of each section. In general, the size of the various sections is about equal to that of the previous edition, covering 1944, except that the section devoted to "Synthetic Rubber" has dropped from 26 pages to only 7 pages. The term "Cellular Rubber" has supplanted that of "Sponge Rubber" used in previous editions. As usual, excellent cross-referenced author and subject indexes make the location of any particular subject or product an easy matter. [From *The Rubber Age* of New York.]

LE CAOUTCHOUC. (RUBBER). By Auguste Chevalier and Jean Le Bras. Published by Presses Universitaires de France, 108 Boulevard Saint-Germain, Paris, France. $4\frac{1}{2} \times 7$ in. 126 pp. (In French).—Issued in 1945, this pocket edition is one of a series of similar books published under the general title of "Que Sais-Je?", designed to furnish basic information on various products, processes and places to students and the general public. It consists of six chapters: (1) History and Natural History of Rubber Plants; (2) Cultivation of Rubber Plants, Especially of the Hevea Variety; (3) Tapping, Coagulation of Latex, and the Preparation of Raw Rubber; (4) Chemistry and Technique of Rubber; (5) The Rubber Industry; (6) Production and Commercial Applications. Jean Le Bras, coauthor of this work, is Research Director of the Institut Français du Caoutchouc. [From *The Rubber Age* of New York.]

REPORT ON MALAYAN AND BRITISH BORNEO RUBBER INDUSTRY. Prepared by E. G. Holt. Available from Superintendent of Documents, Washington 25, D. C. 8×10 in. 72 pp. 25 cents. **REPORT ON NETHERLAND INDIES RUBBER INDUSTRY.** Prepared by E. G. Holt. Available from Superintendent of Documents, Washington 25, D. C. 8×10 in. 64 pp. 20 cents. **REPORT ON INDOCHINA RUBBER INDUSTRY.** Prepared by E. G. Holt. Available from Superintendent of Documents, Washington 25, D. C. 8×10 in. 24 pp. 15 cents.—The reports, which survey the rubber industry in Malaya, British Borneo, Netherlands East Indies, Indochina and Siam (the latter covered in the report on Indochina), were prepared by E. G. Holt, rubber advisor to the Department, as a result of an extensive investigation made on behalf of the Department and the Rubber Development Corporation. During the investigation, Mr. Holt visited the trading centers and accessible producing areas of the Far East in a three-months' tour last summer. The reports contain a review of rubber production rates during 1946 and discuss prospective production for the future. Other phases of the rubber producing industry include the general economy of the countries, political background, currency considerations, estate and native acreage, remilling, equipment, labor, supplies, transportation, production under the Japanese, reoccupation steps, progress in recovery, and rubber stocks. The reports reflect Mr. Holt's usual painstaking efforts. [From *The Rubber Age* of New York.]

PLASTICS HANDBOOK FOR PRODUCT ENGINEERS. Compiled and edited by John Sasso. Published by McGraw-Hill Book Co., Inc., 330 West 42nd St., New York 18, N. Y. 6×9 in. 468 pp. \$6.00.—This is a collection of engineering data on plastics and synthetic rubber. It presents, in concise handbook form, practical and fundamental data of specific use to the engineer planning to adopt these materials to new product designs. Special chapters on the chemistry of plastics and synthetic rubber, designed to give the engineer concise information on the chemical background of the materials, were prepared by Paul O. Powers of the Battelle Memorial Institute. Much of the remaining text has been briefed from material that originally appeared in *Product Engineering*, prepared by qualified authors. As the author points out in his preface, the book is not intended to replace the many available authoritative books and publications, but rather supplements such published data, concentrating on information specifically needed by product engineers.

The book is divided into three parts: (1) Plastic Materials; (2) Design of Plastic Products; (3) Rubberlike Materials: Chemistry and Application. The part on rubberlike materials is subdivided into seven chapters covering

the following subjects: Synthetic Rubberlike Materials, Synthetic Rubbers in Engineering Design, Butyl Rubber, Butadiene-Acrylonitrile Rubbers, GR-S Synthetic Elastomers, Neoprene Rubber, and Thiokol Polysulfide Synthetic Rubbers.

There are 15 chapters in all. In addition to a carefully cross-referenced subject index, there is a bibliography of plastics and lists of reference catalogs on plastics indexed by companies and by materials. [From *The Rubber Age* of New York.]

SPECIFICATIONS FOR GOVERNMENT SYNTHETIC RUBBERS. Effective January 1, 1947. Office of Rubber Reserve, Reconstruction Finance Corp., 811 Vermont Ave., Washington 25, D. C. 63 pages.—This new edition of specifications incorporates the changes necessary to bring it into agreement with developments in the government synthetic rubber program. In the first section on specification limits, specifications for GR-S-38, GR-S-Black-1AC, and GR-A have been eliminated, and those for the newer rubbers added, including GR-S-16, GR-S-17, GR-S-60, GR-S-10-AC, GR-S-40-AC, GR-S-Black-2, and the five types of GR-S latices. Minor changes have been made in the specifications for the older GR-S types, particularly in maximum content of volatile matter. The second section, on sampling, now contains directions for sampling of the GR-S latices. The third section, "Chemical Methods", gives a new method for testing stabilizers. No changes have been made in the fourth section on physical methods except for deletion of the test for viscosity and gelling of GR-S solutions. A new section on latex methods has been added, containing tests on total solids, residual styrene, total soap, pH, surface tension, turbidity, viscosity, and Mooney viscosity of the latex film. A new appendix on weight of total solids in tank cars also has been added. [From the *India Rubber World*.]

MATHEMATICAL THEORY OF ELASTICITY. By I. S. Sokolnikoff. Published by the McGraw-Hill Book Co., 330 West 42nd St., New York 18, N. Y. 6 × 9 in. 373 pp. \$4.50.—The theory of elasticity, in its broad aspects, deals with a study of the behavior of those substances which possess the property of recovering their size and shape when the forces producing deformations are removed. This elastic property is possessed to some extent by all solid bodies, and the prime concern of the mathematical theory of elasticity, with which this book deals, is to reduce to calculations the stresses and strains in an elastic body subjected to the action of a system of prescribed external forces.

The book is divided into five chapters, the first three covering the analysis of strain, the analysis of stress, and stress-strain relations. The fourth chapter, representing the bulk of the book, is devoted to an extensive mathematical treatment of homogeneous beams under tension, torsion and flexure, while the fifth, and concluding, chapter is concerned with the variational methods which find their principal exponent in the theorem of minimum potential energy. The latter chapter contains several procedures for deducing approximate solutions of the boundary-value problems of mathematical physics, these procedures being illustrated by their application to the torsion and flexure problems.

This volume had its origin in a series of lectures given by the author in 1941 and 1942 in the Program of Advanced Instruction and Research in Mechanics, conducted by the Graduate School of Brown University. It includes author and subject indexes, and an appendix containing a summary of the more important formulas used in the text. [From *The Rubber Age* of New York.]

A.S.T.M. STANDARDS ON TEXTILE MATERIALS (with Related Information). Prepared by A.S.T.M. Committee D-13 on Textile Materials. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. October, 1946. Paper, 9 by 6 inches, 490 pages. Price per copy: \$3 to members, \$4 to nonmembers.—This latest edition of textile standards contains 86 specifications, test methods, and tolerances covering a wide range of textile materials. Cotton is represented by 27 standards; rayon and silk are covered by 11 standards. Six standards pertain to asbestos; ten cover wool; four are on bast and leaf fibers; the balance are on general testing methods, definitions, etc. The book also contains a number of appendices, including basic properties of textile fibers; yarn number conversion table; proposed recommended practice for designation of yarn construction; psychrometric table for relative humidity; proposed recommended practice for calculating number of tests to be specified in determining average quality of a textile; proposed method of test for accelerating aging; proposed methods for determining clean wool content, and for evaluating "hand" properties of soft-finished woven fabrics; and American war standard specification and description of color. [From the *India Rubber World*.]

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